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2010 **Jeany Seleti**

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TiO_2 nanoparticles in textile finishing

Rachelapo Jeany Seleti

Supervisor: Assoc. Prof. Jakub Wiener, Msc. PhD

Consultant: Ing. Marie Štěpánková

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Annotation

The aim of this study has been to observe the effect of TiO_2 nanoparticles as it was used in finishing methods such as printing, sol gel and hydrophobic finish. To study the surface wettability of textile fabrics by contact angle measurement .To observe the UV-shielding property of the treated fabrics characterized by UV-VIS spectrophotometry.

The contact angle of textile materials used was measured, the UPF values were also measured and comparable, the porosity of textile material was also determined statistically. With the aims mentioned above the theoretical part was described, the practical method used was also described.

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1 Introduction

The ultraviolet part of solar spectrum (UV) plays an important role in many processes in the biosphere. It has several beneficial effects but it may also be very harmful if the UV radiation exceeds ‘safe’ limits. If the amount of UV radiation is higher or exceeds the so called safe limits, self protection of some biological species is exhausted and the subject may be severely damaged. This includes human organisms, especially their skin and eyes. To avoid damage from high UV exposure, both chronic and acute people should limit their exposure to solar radiation by using protective measures. The solar radiation striking the earth’s surface is characterized by UVB (280-320nm); UVA (320-400nm) wavelengths, UV-C which is totally absorbed by the atmosphere or the ozone layer and does not reach the earth. But the energies of UV-A and UV-B photons that reach the earth surface exceed the carbon-carbon single bond energy of 335kJ/mol, which is why UV radiation is a function of the wavelength of the incident radiation, with the most damage done by radiation less than 300nm. If this erythema effect is multiplied by the intensity of the incident solar light, as a function of wavelength, the wavelengths of maximum danger to skin are 305-310nm. Therefore, to be useful in protecting the wearer from solar UV radiation, textiles must demonstrate effectiveness in the 300-320nm range.

In previous studies it has been observed that high levels of UV radiation in both chronic and acute solar exposure can cause clinical damage, such as sunburn, immune suppression, skin cancers and photo aging, photodermasis (acnes),phototoxic reactions to drugs, erythema (skin reddening),eye damage (opacification of the cornea) and DNA damage. In order to provide protection from UV one of the protective measures to be taken is have knowledge of the factors that contribute to the protective abilities of textiles is vital. Important factors include fiber composition, fabric construction and wet-processing history of the fabric such as color and other finishing chemicals that may have been applied to the textile material.

The effect of ultraviolet radiation on living biological organisms has been extensively studied, and various reporting methods such as UV index, UV protection factor (UPF) and solar protection factor (SPF) have been adopted to create awareness among the general public of the deleterious effects of UV radiations. The UV index is designed to provide the public with a numerical indication of the maximum potential solar UVR level during the day; the higher the number, the higher the solar UVR hazard. The global solar UV Index is a measure of the highest level of UVR every day, and the UVI is calculated using various input parameters such as the ozone level, potential cloud cover, water vapor and aerosols.

To quantify the protective effect of textiles, the solar protective factor (SPF)/ultraviolet protection factor (UPF) is determined. The SPF is the ratio of the potential erythemal effect to the actual erythemal effect transmitted through the fabric by the radiation and can be calculated from spectroscopic measurements. The larger the SPF, the more protective the fabric is to UV radiation. Typically, a fabric with an SPF of > 40 is considered to provide excellent protection against UV radiation (according to AS/NZS 4399: sun protective clothing evaluation and classification, standard Australia, Sydney).

When radiation strikes a fiber surface, it can be reflected, absorbed, transmitted through the fiber or pass between fibers. Radiation reflected, absorbed or transmitted depend on many factors, including the fiber type, the fiber surface-smoothness, the fabric factor (the fraction of the surface area of the fabric covered by yarns) and the presence or absence of fiber delustrants, dyes and UV absorbers. In this diploma work the surface wettability and topology of textile fabrics were studied by contact angle measurement .The UV-shielding property of the treated fabrics was also characterized by UV-VIS spectrophotometry. Different fiber materials such as polyester, cotton, wool, glass fiber, and Kevlar rough surface and Kevlar smooth surface were treated and the utilized method for treatment was hydrophobic treatment. And for cotton fiber the sol gel method was done to analyze the contact and the UV shielding properties of the fiber material, and also wool, Kevlar, polyester, glass fiber and cotton were treated by TiO_2 nanoparticles by hydrophobic finish. The results were obtained, comparing the effect of different TiO2 powder using the finishing treatment, comparing their effect on surface wettability and UV protection abilty.

2 Theoretical part

2.1 Solar Radiation

Solar radiation is an important natural factor because it forms the Earth's climate and has a significant influence on the environment. The ultraviolet part of the solar spectrum (UV) plays an important role in many processes in the biosphere. It has several beneficial effects but it may also be very harmful if UV exceeds "safe" limits. If the amount of UV radiation is sufficiently high the self-protection ability of some biological species is exhausted and the subject may be severely damaged. This also concerns the human organism, in particular the skin and the eyes. To avoid damage from high UV exposures, both acute and chronic, people should limit their exposure to solar radiation by using protective measures. The solar radiation striking the earth's surface is composed of light waves with wavelengths ranging from the infrared to the UV radiation. The table below is showing the wavelengths, relative intensities and average photon energies of this radiation. [1]

Table 1 Characteristics of solar radiation striking the earth's surface

Classification	Wavelength (nm)	Relative Intensity	Average photon energy (kj/mol)
UV-B radiation	280-320	0.5	400
UV-A1 radiation	320-360	2.4	350
UV-A2 radiation	360-400	3.2	315
Visible radiation	400-800	51.8	200
Infrared radiation	800-3000	42.1	63

Although the intensity of UV radiation is much less than visible or infrared radiation, the energy per photon is significantly higher. The very high energy of the UV-C photons is mostly absorbed by ozone in the higher regions of the atmosphere decreasing their relative intensity on the earth surface to almost zero. But the energies of UV-A and UV-B photons that reach the earth surface exceed the carbon-carbon single bond energy of 335kJ/mol, which is why UV radiation is a function of the wavelength of the incident radiation, with the most damage done by radiation less than 300nm. If this erythema effect is multiplied by the intensity of the incident solar light, as a function of wavelength, the wavelengths of maximum danger to skin are 305-310nm. Therefore, to be useful in protecting the wearer from solar UV radiation, textiles must demonstrate effectiveness in the 300-320nm range. [1]

Acute as well as chronic sun exposure is well known to induce biological and clinical damage, such as sunburn, immune suppression, skin cancers and photo aging, photodermasis (acnes),phototoxic reactions to drugs, erythema (skin reddening),eye damage (opacification of the cornea) and DNA damage. UVB radiation, which includes the most energetic photons, participates in all of these damages, and can induce direct DNA lesions such as cyclobutane pyrimidine dimers (CPD) and 6, 4 pyrimidine pyramid one. Subsequent mutations are involved in the development of UV-induced skin cancers. However, although UVA radiation is less energetic than UVB, it accounts for at least 95% of the solar UV irradiance received at ground level. Recent studies pointed out their role in immune-suppression, photo aging and mutagenesis. For this reason, the new generation of sunscreens has to provide an efficient protection against UVA as well as UVB radiation [2&3]

Solar UV radiation reaching earth is a combination of UVB (280-320 nm) and UVA (320-400 nm) wavelengths. UV-C is totally absorbed by the atmosphere or the ozone layer and does not reach the earth. UV-A causes little visible reaction on the skin but has been shown to decrease the immunological response of skin cells. UV-B is most responsible for the development of skin cancers. Other than drastically reducing exposure to the sun, the most frequently recommended form of UV protection is the use of sunscreens, hats, and proper selection of clothing. Unfortunately, one cannot hold up a textile material to sunlight and determine how susceptible a textile is to UV rays. Even textiles which seem to be non-light transmitting may pass significant amounts of erythema-inducing UV irradiation. Therefore, knowledge of the factors that contribute to the protective abilities of textiles is vital. Important factors include fiber composition, fabric construction and wet-processing history of the fabric such as color and other finishing chemicals that may have been applied to the textile material [8].

The assessment of the efficiency of a sunscreen is primarily based on the value of its sun protection factor (SPF), which reflects the protection against erythema. In the skin erythemal response, the actual contribution of UVA wavelengths represents only a small percentage. In addition, numerous biological damages induced by sun exposure occur at doses lower than that inducing erythema, especially in repeated exposure condition. Therefore, the SPF value, which is still the only regulatory requested protection factor for sunscreen products, does not seem sufficient to reflect the efficiency of protection against all biological end-points induced by the entire solar UV spectrum. For example the protective effect of sunscreens on UV-induced immune suppression has been largely assessed. The evaluation of products filtering both UVB and UVA radiation have been shown to afford a better protection with regard to photo aging markers, than preparations that absorb mostly in the UVB range. It has also been suggested that the development of basal cell carcinoma in sunscreens users may be due to poor absorption of the sunscreens used in the UVA waveband [9].

2.2 Solar UV index, UV protection factor and solar protection factor

The effect of ultraviolet radiation on living biological organisms has been extensively studied, and various reporting methods such as UV index, UV protection factor (UPF) and solar protection factor (SPF) have been adopted to create awareness among the general public of the deleterious effects of UV radiations. At a given wavelength, electromagnetic radiation may be reflected, absorbed or transmitted by any given object. If the response of the system at each wavelength is a linear function of the dose, then the response (R) by a broad spectrum is given by the following formula:

$$R = \int_{t_1}^{t_2}\int_{\lambda_1}^{\lambda_2} \sigma(\lambda) I(\lambda, t)\, d\lambda\, dt \qquad (1)$$

Where I (λ, t) is the irradiance at wavelength λ; t is time and σ (λ) is the cross-section for eliciting this response at wavelengths λ. The changes in the spectrum have been covered by including time as an argument of the irradiance function and as a variable of integration. The UV index is designed to provide the public with a numerical indication of the maximum potential solar UVR level during the day; the higher the number, the higher the solar UVR hazard. The global solar UV Index is a measure of the highest level of UVR every day, and the UVI is calculated using various input parameters such as the ozone level, potential cloud cover, water vapor and aerosols. The UV index is reported as the maximum biologically effective solar average UVR (UVR_{eff}) for the day, and is an average taken over either 10 or 30 minutes. The UVR is usually highest around midday but the temperature is often highest later in the afternoon. UVR index values are grouped into five exposure categories from low to extreme with different color codes. [12]

To quantify the protective effect of textiles, the solar protective factor (SPF) is determined. The SPF is the ratio of the potential erythemal effect to the actual erythemal effect transmitted through the fabric by the radiation and can be calculated from spectroscopic measurements. The larger the SPF, the more protective the fabric is to UV radiation. In Europe and Australia, the SPF is referred to as ultraviolet protection factor (UPF). The SPF is also used with so called 'sun blocking' skin creams, giving a relative measure of how much longer a person can be exposed to sunlight before skin damage occurs. Typically, a fabric with an SPF of > 40 is considered to provide excellent protection against UV radiation (according to AS/NZS 4399: sun protective clothing-evaluation and classification, standard Australia, Sydney). It is possible to realize 80% of the theoretical maximum of SPF 200.Since the most probable time for long term solar exposure is in the summer, the most likely candidates for UV protective finishes are lightweight woven and knitted fabrics intended for producing shirts, blouses, t-shirts, beach wear, swim wear, sportswear, and others. Industrial fabrics designed for awnings, canopies, tents and blinds may also benefit from UV protection treatment [1]

2.3 Mechanism of UV protection

When radiation strikes a fiber surface, it can be reflected, absorbed, transmitted through the fiber or pass between fibers. The relative amount of incident radiation strikes the fiber or fibers as follows;

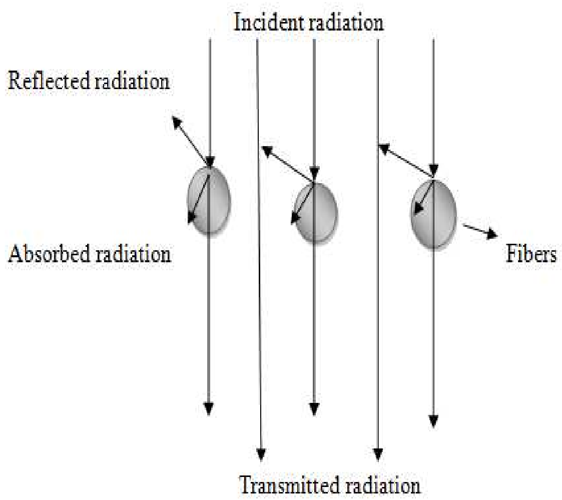


Figure 1 Radiation in contact with a textile surface

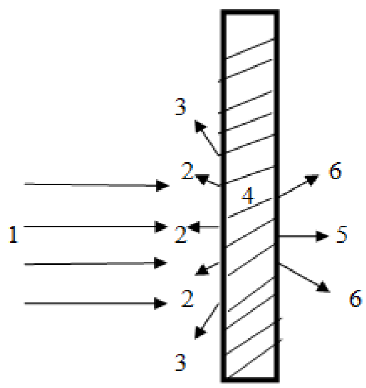


Figure 2 Model of fabric–light interactions

Where 1.normal incident (I), 2.Regular reflection (dr), 3. Scattered reflection (sr), 4. absorption, 5.direct transmission (dt), 6.diffuse transmission (st). Radiation reflected, absorbed or transmitted depend on many factors, including the fiber type, the fiber surface-smoothness, the fabric factor (the fraction of the surface area of the fabric covered by yarns) and the presence or absence of fiber delustrants, dyes and UV absorbers. [1& 2]

2.3.1 The effect of fiber type on the SPF of fabrics of similar construction

Table 2 Solar protection factors (SPF) of fabrics

Fabric description	Approximate SPF
Cotton tricot	4
Wool tricot	45
Silk twill	7
Polyester tricot	26
Nylon/elastomer 80/20 tricot	12

Cotton and silk fibers offer little protection to UV radiation can pass through without being markedly absorbed. Wool and PES on the other hand, have significant higher SPF’s since these fibers will absorbs UV radiation. Nylon falls in between these extremes. One factor influencing nylon and PES absorbance is the presence of the delustrant TiO_2, a material that strongly absorbs UV radiation. If fibers absorb all of the incident radiation, then the only source of transmitted rays is from the spacing between yarns. By definition, the theoretical maximum SPF is the reciprocal of one minus the cover factor.

$$\mathbf{SPFmax} = \frac{\mathbf{1}}{\mathbf{1 - cover\ factor}} \qquad (2)$$

The equation above illustrates the relationship between the maximum SPF and the cover factor. Using the SPF value of 50 as the goal, a fabric with a cover factor of 0.98 and composed of fibers that absorbs all of the non-reflected UV radiation will provide its wearer with excellent protection against solar UV radiation. Of course tight micro-fibers provide a better UV protection than fabrics made from normal sized fibers with specific weight and type of construction. [1]

2.4 UV exposure and human skin

Human skin reconstructed in vitro, composed of both a living dermal equivalent and a fully differentiated epidermis, permitted the identification of tissue specific damages induced by either UVB or UVA radiation. Epidermal keratinocytes were preferentially targeted by UVB, while UVA induced major alterations in the dermal compartment. Taking advantage of these specific damages and the possibility of applying topical sunscreens on the skin surface, the efficiency of single absorbers has been tested. Other studies using organotypic cultures confirm their usefulness in the evaluation of photo protection [14].

In terms of sensitivity to light and tendency to pigmentation, there are 6 basic types of skin that demand different levels of UV protection as shown in the following table:

Table 3 Effect of UV rays on different types of skin

Skin type (Appearance	Critical dose mJ/cm2	Self protection time (min)	Risk level
I - White	15 – 30	5 - 10	Burns easily, has the highest risk of
II - White	25 – 35	8 - 12	Burn and only rarely tan
III - Brownish	30 – 50	10 - 15	Tan and occasionally burn
IV - Brown	45 – 60	15 - 20	Tan and occasionally burn
V - Brown	60 – 100	20 - 35	Sufficient levels of melanin and rarely
VI – Dark Brown	100 – 200	35 - 70	Sufficient levels of melanin pigment

The minimal erythemal dose (MED) is apparently consistent with a fair complexion, but shows variations among people of types III and IV. For practical purposes, the population could be classified into two main groups, sensitive and less sensitive individuals [11].

Factors that affect solar UVR include cloud cover, the sun's altitude, geographical position, altitude, ozone layer, scattering in the atmosphere, environmental and related conditions. Much research has been carried out to assess the impact of the UV rays on various living organisms, especially humans and the relationship between skin cancer and UV dosage is well correlated. Changes in leisure behavior, which has led to more frequent sun exposure, are one of the major reasons for malignant cutaneous melanoma. Skin cells that receive sunlight absorb harmful UV radiation, and slough off to excrete harmful UV from the body. But the absorption of too much UVR leads to scars that can induce diseases like skin cancer. Excessive UV radiation leads to cell damage and causes inflammation of human skin, the obvious consequences of which is erythema or sunburn. The reciprocal value of these cuticle radiation doses is called erythema effectiveness whose maximum occurs at 308 nm. The total UVR dose reaching the skin is an important factor in the occurrence of both erythema and skin cancer, although there is no proven link between erythema and skin cancer [14&15].

2.4.1 Ultraviolet Protection Factor Determination

The ultraviolet protection of a fabric is expressed by the Ultraviolet Protection Factor, UPF. For sun creams, the Sun Protection factor (SPF) is used. The UPF evaluates the reduction in the amount of the UV radiation that passes through the fabric to the skin. For example, when a fabric has an UPF of 20, only 1/20th of UV radiation reaches the skin.

To determine the in vitro UPF, the spectral irradiance (of the source and transmitted spectrum) is weighted against the erythemal action spectrum, as follows;

$$UPF = \frac{\int_{290}^{400} E_\lambda \, S_\lambda \, d_\lambda}{\int_{290}^{400} E_\lambda \, S_\lambda \, T_\lambda \, d_\lambda} \qquad [3]$$

Where λ is the wavelength in nm; *E*, relative erythemal spectral effectiveness; *S*, solar spectral irradiance of the source in watts per square meter;

d, bandwidth in nanometer; and

T, spectral transmission of the sample. The integrals (∫) are calculated over the wavelength range of 290 to 400 nm.

And/or also to calculate UPF, risk estimates for unprotected skin are obtained by multiplying the solar spectral source with the CIE erythemal action spectrum at each wavelength interval, $\Delta\lambda$ and summing the response over all relevant wavelengths. In the spectrometer, transmittance data are normally collected at 2- or 5nm intervals, usually between 290-400nm.

$$\text{Risk}_{\text{unprotected}} = \sum S(\lambda).\,A(\lambda).\,\Delta\lambda$$

Where $S_{(\lambda)}$ is the source of spectrum in $W.m^{2}.nm^{-1}$; $A_{(\lambda)}$ is the action spectrum for the measured response (dimensionless) and $\Delta\lambda$ is the bandwidth in nm, determining by the experimental conditions of the measurement. Risk estimates for the fabric protected skins are obtained by multiplying the risk at each wavelength by the transmittance of the fabric at each wavelength, $T_{(\lambda)}$ and summing over the same wavelengths.

$$\text{Risk}_{\text{protected}} = \sum S(\lambda).\,A(\lambda).\,T(\lambda).\,\Delta\lambda$$

Finally the UPF is calculated from the two equations as follows;

$$\text{UPF} = \text{Risk}_{\text{unprotected}} / \text{Risk}_{\text{protected}}$$

Analogous to the sun protection factor of sunscreens, UPF is defined as the ratio of the average effective UV irradiance calculated for unprotected skin to the average effective UV irradiance calculated for skin protected by the test fabric. Inter-comparison measurements of different testing laboratories have shown that spectrophotometry is an accurate and reproducible test method for determining UPF, particularly for samples with UPFs below 50. However, UPFs of 50 and higher are only of theoretical interest, as even in Australia the maximum daily UV exposure is about 35 minimal erythema doses

(MED's). Ultraviolet transmission measurements of textiles are generally made under worst-case conditions, with collimated radiation at right angles to the fabric. Thus, the actual UV protection of a particular textile would always be greater than the measurement obtained using spectrophotometer. [19]

Since the relative erythemal spectral effectiveness is higher in the UV B region compared to the UV A region, the UPF values depend primarily on the transmission in the UV B region. UV rays falling on textiles are partly reflected, absorbed and partly transmitted through the fibers & interstices, and the optical porosity of a fabric limits its potential to provide protection against UVR. The solar protection factor (SPF) is defined as a quotient from a harmful dose without, and a harmful dose with, sun protection. This can be calculated from erythemal effectiveness (EW (λ)), (P(λ)) and from the wavelength dependent transmission of the sun protection agent. The difference between the values of UPS and SPF arises mainly because of the 'hole effect' in the fabrics. The UV radiation transmitted through a textile fabric consists of the waves that pass unchanged through the pores of the fabric and scattered waves that have interacted with the fabric. Many research studies were conducted to establish the parameters that affect the UV permeability of the textile garment. Some studies concluded that the compactness and the weight of the fabric are the most relevant parameters, while others claim that dark color shades offer more protection, [18&19].

2.5 Effect of UV radiation on textile materials

UV radiation is one of the major causes of degradation of textile materials, which is due to excitations in some parts of the polymer molecule and a gradual loss of integrity, and depends on the nature of the fiber. Because of the very large surface volume ratio, textile materials are susceptible to influences from light and other environmental factors. The penetration of UVR in nylon causes photo oxidation and results in decrease in elasticity, tensile strength and a slight increase in the degree of crystallinity.

In the absence of UV filters, the loss in tensile strength appears to be higher in the case of nylon (100% loss), followed by wool, cotton and polyester, with approximately 23%, 34% and 44% respectively after 30 days of exposure. Elevated temperature and UVB radiation on cotton plants result in severe loss of bolls. Naturally-colored cottons contain pigment ranges from light green to tan, brown and inherent long-term UV protection properties with a UPF of 64 and 47, whereas normal cotton shows a UPF of 8. [20]

2.6 UV absorbers

UV absorbers are organic or inorganic colorless compounds with strong absorption in the UV range of 290 – 360 nm. UV absorbers incorporated into the fibers convert electronic excitation energy into thermal energy, function as radical scavengers and singlet oxygen quenchers. The high-energy, short-wave UVR excites the UV absorber to a higher energy state; the energy absorbed may then be dissipated as longer-wave radiation. Alternately, isomerisation can occur and the UV absorber may then fragment into non-absorbing isomers. Sunscreen lotions contain UV absorbers that physically block UVR. The most widely used UVB screens, 2-ethylhexyl-4-methoxy cinnamate with high refractive index, make a substantial contribution to the RI matching of skin, i.e. ‘refractive index matching’. An effective UV absorber must be able to absorb throughout the spectrum, to remain stable against UVR, and to dissipate the absorbed energy to avoid degradation or loss in color.

Organic UV absorbers are mainly derivatives of o-hydroxy benzophenones, o-hydroxy phenyltriazines, o-hydroxy phenyl hydrazine’s. The orthohydroxyl group is considered essential for absorption and to make the compound soluble in alkaline solution. Some of the substituted benzophenones penetrate into synthetic fibres much like disperse dyes. Commonly-used UV absorbers are 2-hydroxy benzophenones, 2-hydroxy phenyl benzotriazoles, 2-hydroxy phenyl-Striazines and chemicals such as benzoic acid esters, and hindered amines. The strong absorption in the near UV of 2, 4 dihydroxy benzophenone is attributed to conjugating chelation between the orthohydroxyl and carbonyl groups. Organic products like benzotriazole, hydro benzophenone and phenyl triazine are primarily used for coating and padding processes in order to achieve broad protection against UV rays. Suitable combinations of UV absorbers and antioxidants can yield synergistic effects. Benzophenone derivatives have low energy levels, easy diffusibility and a low sublimation fastness. Orthohydroxy phenyl and diphenyl triazine derivatives have an excellent sublimation fastness, and a self-dispersing formulation can be used in high temperature dyeing in pad baths and also in print pastes [21].

UV absorbers incorporated into the spinning dope prior to the fiber extrusion and dye bath in bath dyeing improve the light fastness of certain pastel shades and the weather ability spun-dyed fibers. UV absorbers to the extent of 0.6 – 2.5% are sufficient enough to provide UVR protection fabrics. The presence of UV absorbers in polyester, nylon, silk and wool protects the fibers against sunlight-induced photo degradation. On wool, UV absorbers can retard the photo-yellowing that occurs upon exposure to sunlight. Triazine class-hindered amine light stabilizers are used in polypropylene to improve the UV stability. The addition of HALS to 0.15% weight is sufficient to improve stability substantially. Even pigmented PP requires UV stabilizers if the fibers are exposed to UV during their services. High-energy UV absorbers suitable for PET include derivatives of o-hydroxy phenyl diphenyl triazine, suitable for dye baths, pad liquor or print paste. UV absorbers have refractive indices of about > 2.55, by means of which maximum covering capacity and opacity is achieved [11].

The presence of inorganic pigments in the fibers results in more diffuse reflection of light from the substrate, and provides better protection. TiO_2 added in the spinning dope for matt effects in the fibers also acts as a UV absorber. Titanium dioxide and ceramic materials have an absorption capacity in the UV region between 280 and 400 nm, and reflects visible and IR rays; these absorbers are also added as dope additives. For maximum effect, the particles have to be mono molecularly distributed, and are often applied in one bath. Nano scale titanium gel particles strongly bound to the cotton fabrics can give a UPF ≥ 50 without impairing the tensile properties. Brighter viscose yarns provide the highest UV transmittance compared to the dull pigmented viscose yarns, modal yarns. Zinc oxide nano particles, which have a very narrow size distribution (20-40 nm) and minimal aggregation, can result in higher levels of UV blocking. Use of TiO_2, ZnO alone produces less absorption of UVR than a mixture of (67/33) titanium dioxide and zinc oxide on cotton and nylon fabrics. Microfine nylon fabrics with a porosity of 0.1% are capable of giving UPF > 50 with 1.5% TiO_2. Incorporating UV absorber in dyeing decreases the dye uptake slightly, except in post-treatment application [21]

Many commercial products and processes have been developed to produce fabrics with a high level of UPF using various dope additions and topical applications for almost all types of fabrics produced from cellulosic fibers, wool, silk and synthetic fibers. Most of the commercial products are compatible with the dyes and other finishing agents applied to the textile materials, and these agents can be applied using simple padding, the exhaust method, the pad thermo fix and the pad-dry-cure methods [19&21]

2.7 Textile materials and UV protection

Sun protection involves a combination of sun avoidance and the use of protective garments &accessories. Reducing the exposure time to sunlight, using sunscreens and protective clothes are the three ways of protection against the deleterious effects of UV radiation. Apart from sunscreen lotions, textile materials and accessories made of textile materials are largely used for UV protection. UV protection through textiles include various apparels, accessories such as hats, shoes, shade structures such as umbrellas, awnings, and baby carrier covers and the fabric materials to produce these items. [20]

2.8 Nature of fibers

In textiles, UPF is strongly dependent on the chemical structure of the fibers. The nature of the fibers influences the UPFs as they vary in UV transparency. Natural fibers like cotton, silk, and wool have lower degree UVR absorption than synthetic fibers such as PET. Cotton fabric in a grey state provides a higher UPF because the natural pigments, pectin, and waxes act as UV absorbers, while bleached fibers have high UV transparency. Raw natural fibers like linen and hemp possess a UPF of 20 and 10 to 15 respectively, and are not perfect UV protectors even with lignin content. However; the strong absorption of jute is due to the presence of lignin, which acts as a natural absorber. Protein fibers also have mixed effects in allowing UV radiation. Dyed cotton fabrics show higher UPF, and undyed, bleached cotton yields very poor UPF values. Wool absorbs strongly in the region of 280 – 400 nm and even beyond 400 nm. Exposure to sunlight damages the quality of silk's color, strength and resiliency in both dry and wet conditions. Mulberry silk is deteriorated to a greater extent than muga silk. Bleached silk and bleached PAN show very low UPFs of 9.4 and 3.9 respectively. Polyester fibers absorb more in the UVA & UV B regions than aliphatic polyamide fibers. [17&18]

A wide variety of synthetic and naturally occurring high polymers absorb solar ultraviolet radiation and undergo photolytic, photo-oxidative, and thermo-oxidative reactions that result in the degradation of the material. The degradation suffered by these materials can range from mere surface discoloration affecting the aesthetic appeal of a product to extensive loss of mechanical properties, which severely limits their performance. The deleterious effects of solar UVB radiation in particular, on wood, paper, biopolymers, and polymers *(*plastics and rubber*)*, are well known. The phenomenon is of special interest to the building industry, which relies on polymer building products that are routinely exposed to sunlight during use. Most of the common polymers used in such applications contain photo stabilizers to control photo damage and to ensure acceptable lifetimes under outdoor exposure conditions. [18]

2.9 Moisture and swelling

The ability of textile fibers to provide UV protection varies depending upon the structure and other additives present in the fibers. Besides, the construction parameters and wear conditions of the textile materials, moisture and additives incorporated in processing also affect the UPF of the textile materials. In the case of moisture, the influence largely depends on the type and hygroscopicity of fibers, as well as conditioning time, which result in swelling phenomena.

[15]

The moisture content affects the UPF of the fabric in two ways, namely the swelling of fibers due to moisture absorption, which reduces the interstices, and consequently the UV transmittance. On the other hand, the presence of water reduces scattering effects, as the refractive index of water is closer to that of the textile polymer, and hence there is a greater UV transmission vis-à-vis a lower UPF. A typical cotton fabric could transmit 15-20% UVR; rising to more than 50% if the garment is wet. For adequate protection, the UVR transmission should be lower than 6% and 2.5% for extremely good protection. Dependence of humidity is more pronounced in silk and viscose, of which viscose has a higher water absorption and swelling capacity, while silk has poor swelling properties. Even though silk has poor swelling properties, it's very fine nature and a greater number of fibers in the cross-section of yarn results in higher swelling due to capillary absorption, and in turn less UV transmittance. Finishing treatments given to the fabrics to reduce swelling reduce the transmittance of UV rays. In general, hygroscopic fibers and their UPF show better correlation [15]

2.10 Fabric construction factors

When the ultraviolet radiation hits the textile materials, different types of interactions occur depending upon the substrate and its conditions. The UV protection by textile materials and apparel is a function of the chemical characteristics, physico-chemical type of fiber, presence of UV absorbers, construction of fabric, thickness, porosity, extension of the fabric, moisture content of the fabrics, color and the finishing given to the fabric. A part of the radiation is reflected at the boundaries of the textile surface. The UVR transmitted through textile fabrics consists of the unchanged waves that pass through the interstices of the fabrics as well as scattered waves that have interacted with the fabrics. Another part is absorbed when it penetrates the sample, and is converted into a different energy form. The portion of radiation that travels through the fabric and reaches the skin is appropriately referred to as the 'transmission component' [15]

The UPF increases with fabric density and thickness for similar construction, and is dependent on porosity (UPF = 100 / porosity). A high correlation exists between the UPF and the fabric porosity but is also influenced by the type of fibers. The relative order of importance for the UV protection is given by % cover > fiber type > fabric thickness. Cloth cover does not consider the flatness of the yarns, which might result in a higher cloth cover than the calculated value. A UPF with fabric weight and thickness shows better correlation than cloth cover. Therefore fabrics with the maximum number of yarns in warp and weft give high UPFs. UPF values of 200, 40, 20 and 10 can be achieved with the percentage cover factors of 99.5, 97.5, 95 and 90 respectively [18].

The percentage UVR transmission of a fabric is related to the fabric cover factor by (100 – cover factor) and the UPF is given by UPF = 100 / (100-CF). To achieve a minimum UPF rating of 15, the cover factor of the textile must be greater than 93%, and a very small increase in CF leads to substantial improvements in the UPF of the textiles above 95% cover factor. In the case of terry cloth, a high variability in UPF exists due to irregularities in the fabric construction. Woven fabrics usually have a higher cover factor than knits due to the type of construction. Thick rib structures of hemp and linen can allow10.52 – 12.70% and 9.03 – 11.47% of UV A and UV B respectively. However, knitted structure made from a blend of synthetic fibers with Lycra offers the best protection against solar radiation, and warp-knitted blinds are capable of screening up to 80% of the solar radiation and bright glares. Stretching reduces the UPF rating of the fabric during wear, as the effective cover factor is reduced. However, the cover factor can be modified through many dry finishing processes through overfeed on the stenter, compressive shrinkage processes such as compacting and sanforising, which are normally used to obtain dimensional stability, incidentally increasing the cover factor and hence the UPF. Gentle milling employed in the case of lightweight wool fabrics can also enhance the cover factor and the UPF [18&20].

2.11 Dyeing and finishing

Depending upon the type of dye or pigment, the absorptive groups present in the dyestuff, depth after dyeing, the uniformity and additives, the UV protection abilities of the textile materials are considerably influenced. In a given fabric, higher transmission of UV radiation is observed in the case of bright fibers (viscose) than dull fibers. A protective effect can be obtained by dyeing or printing, which is better than using heavyweight fabrics which are not suitable for summer conditions. Darker colors of the same fabric type (black, navy, dark red) absorb UVR much more strongly than the light pastel colors for identical weave with UPF, in the ranges of 18 – 37 and 19 – 34 for cotton and polyester respectively. Some direct, reactive and vat dyes are capable of giving a UPF of 50 plus [21]

Some of the direct dyes substantially increase the UPF of bleached cloth, which depends on the relative transmittance of the dyes in the UV B region. In many cases, a UPF calculated using a direct dye solution appears to be higher than that of the fabric after dyeing, mainly because the actual concentrations are mostly less than the theoretical concentration. Dyes extracted from various natural resources also show the UPF within the range of 15 – 45 depending on the mordant used . Cellulosic fabrics transmit UV A and UV B equally with the transmittance ratio (TA/TB) 0.9. When dyed with the reactive dyes, the UPF increases from 4.7 to 5.0 – 14.0 depending upon the concentration, which is not sufficient to satisfy the minimum requirements [60]. Some of the vinyl sulphone dyes and monochlorotriazine dyes possess UVR absorption characteristics, which also increase with the concentration. Cellulosic fabrics dyed with these dyes show reduced UVR transmission from 24.6% to 10-20% and 27.8% to 8-22% for UV A and UV B respectively. When mixtures of these dyes are used, the UPF increases synergistically. Some combinations of disperse reactive mix can give prolonged UV protection with a UPF of 50+ for P/C blends [3&14].

Optical brightening agents or fabric whitening agents are used at the finishing operations, as well as in the wash cycles, and their effect on UPFs has been demonstrated extensively in the past. Optical brightening agents are often applied to enhance the whiteness of textiles by UV excitation and visible blue emission. The phenomenon of excitation and emission is caused by the transition of electrons involving p-orbital's from either conjugated or aromatic compounds. Most optical brighteners have excitation maxima within the range of 340 – 400 nm. OBA can improve the UPF of cotton and cotton blends, but not of fabrics that are 100% polyester or nylon. The presence of OBA in the P/C blends (67/33) to the extent of 0.5% can improve the UPF from 16.3 to 32.2, which is more or less closer to that obtained using the UV absorbers with 0.2% (UPF 35.5). Washing the fabrics leads to a loss of UPF in the case of OBA-treated fabrics, and the UPF reaches the level of that in untreated fabric after 10 washes, which shows the semi-permanent nature of the finish and protection. Another limitation of many OBAs is that they mostly absorb in the UVA part of the day light spectrum (93%) but have a weak absorption in UV absorption around 308 nm (92%), which plays an important role in skin disease [19&16].

2.12 UPF measurement systems

Appropriate precautions which were applied while carrying out the measurement should be sufficient to collect all the scattered and transmitted lights through an integrating sphere, to include all the erythemal active wavelengths (UVA & UVB) spectral measurements without any influence of fluorescence from FWA, if it is present in the fabric. There are currently 12 sites in Australia and Antarctica installed with broadband UVR detectors to measure the total energy received over a range of wavelength in UVR region in both direct and diffuse radiation. Polysulphone films have been widely used in the construction of personal dosimeters, which absorb strongly in the UV B region [5& 21].

The instrument for measuring fabric transmission includes broadband radiometers, spectroradiometers, or spectrophotometers, and Xenon lamps. Filters are placed next to the test specimen to prevent the effects of fluorescence reaching the integrating sphere. The spectral response of the detector is also important in determining system performance, and it must be capable of detecting UVR accurately and linearly over a very large range of intensities and discriminating the signal from the detector dark current. Many commercial systems have difficulty in measuring UPFs above 100 due to dynamic range, dark current discrimination at lower wavelengths of <300 nm, and fluorescence at wavelengths of >380 nm. [5& 7]

Low light levels in the UVR source used for measurement can also lead to difficulty in distinguishing between the transmitted UVR and the natural dark current of the detector. The measurement of UPF on a clothing material can be carried out by measuring the diffuse spectral transmittance in vitro or by measuring the increase in exposure time required to induce erythema sun burn in vivo. The preparation of the fabric prior to the UV transmission test includes the exposure of specimen to laundering, simulated sunlight and chlorinated pool water, and to present in a state that simulate the conditions at the end of two years of normal seasonal use, so that the UV protection level finally stated on the label estimates the maximum transmittance of the garment fabric during a two-year life cycle [16& 19]

2.13 UV protection care labeling

Initiatives for developing standards related to UV protection started in the 1990s, and standards related to the preparation of fabrics, testing and guidance for UV protection labelling have been formulated by different agencies. Care labelling similar to fabric and garment care labels has been developed for UV protection, and standard procedures have been established for the measurement, calculation, labeling methods and comparison of label values of textile products. Since 1981, the Skin Cancer Foundation, an international body, has offered a Seal of Recommendation for the photo-protective products which includes sunscreens, sunglasses, window films and laundry detergent additives, in accordance with AATCC TM 183 or AS/NZS 4399; the products recommended are reviewed annually [12].

Table 4 Grades and classification of UPF

UPF	Transmissions %	Classification	Grade
> 40	< 2.5	Excellent protection	III
30-40	3.3 – 2.5	Very good protection	II
20-29	5.0 – 2.4	Good protection	I

UV labeling is an additional requirement besides other labeling requirements of garments including Permanent Care Labels and Fiber Content labels. Apart from the UPF label, block numbers can also be used based on the UV transmittance value in their respective UVR range. Table 4 shows the various grades and the related protection factors for the textile materials. The UPF value to be placed on the label is that of the sample, reduced by its standard error of UPF values, and then rounded down to the nearest multiple of 5 but not greater than 50. A UPF of 20 means that 1/20th, i.e. 5%, of the biologically effective UV radiation striking the surface of the fabric actually passes through it [17].

2.14 Textile qualities and UV protection

2.14.1 Material

Summer clothing is usually made of cotton, viscose, rayon, linen, polyester, or combinations thereof. Other types of materials, such as nylon or elastane, are also found in bathing suits, nylon stockings, and other garments. Consumers generally consider lightweight non-synthetic fabrics (cotton and linen) to be the most comfortable for summer wear. Comparison of the UPF of different types of material is difficult and possible only in limited situations. This is because certain production steps (dyeing and finishing) vary based on the material, resulting in a comparison of the "material-color-finish" combination and not of the material itself. In the case of synthetic fibers, such as polyester and polyamide, an analysis is even more difficult because the UV protection of these materials depends on the type and quantity of additives to the fiber, such as antioxidants or UV stabilizers. [20]

In accordance with most studies, the type of fiber used to construct a textile can have a substantial effect on the UPF, especially for white and non-dyed fabrics. Bleached cotton and viscose rayon are transparent to UV radiation and thus provide relatively low UV protection. It was reported that bleached cotton print cloth had a UV transmission of 23.7%, whereas the same unbleached fabric had a UV transmission of only 14.4%. The effect of bleaching was also evident among silk fabrics in their study. Compared with bleached textiles, unbleached fabrics such as cotton and silk have better UV protective properties due to UV-absorbing natural pigments and other impurities. Polyester usually has good UV blocking properties, as this fabric allows relatively little UV-B transmission, probably because of the large conjugated system of polymer chains. Polyester (or polyester blends) may be the most suitable fabric type for UV protective garments (Table 5). However, its permeability for wavelengths in the UV-A range is frequently higher than that of other fiber types; this could be of significance for wearers with polymorphic light eruption, solar urticaria, chronic actinic dermatitis, or actinic prurigo. [19&21]

Table 5 Summary of Factors Significantly Affecting the UPF of Apparel Textiles

Fabric material	UPFs of cotton, linen, rayon, viscose are usually smaller than UPFs of wool, silk, nylon and PES provides usually high UPFs.
Fabric porosity, weight and thickness	UPFs increases with increasing yarn-to-yarn space, and increasing fabric weight and thickness.
Fabric colors	UPF increases with dark colors
UV absorbers	UPF is improved by UV absorbers.
Stretch	UPF decreases under stretch
Wetness	UPF decreases when cotton becomes wet
Washing	UPF increases for cotton fabrics

2.14.2 Porosity, Weight, and Thickness

Researchers have referred to fabric porosity by a variety of terms, including cover factor, tightness of weave, and fabric openness. Cover factor may be defined as the percentage area occupied by warp and filling yarns in a given fabric area. To understand the relationship between UV transmission and fabric structure, an "ideal" fabric is proposed, in which the yarns are completely opaque to UV radiation and the holes or spaces between the yarns are very small. Ultraviolet transmission through ideal fabric is related to the cover factor of the fabric with opaque yarns as follows:

$$\% \text{ UV transmission} = 100 - \% \text{ cover factor}$$

Fabric construction is the primary determinant of fabric porosity, followed by fabric weight. The closer the weave or knitting, the less UV radiation is transmitted. Spaces between the yarns are generally larger in a knit fabric than in a woven textile, and plain woven textiles have a lower porosity than textiles woven using other weaves. An increase in weight per unit area also decreases fabric porosity. The spaces between the yarns are smaller in heavier textiles, permitting transmission of less UV radiation. However, yarns are usually not opaque to UV radiation; thus, UPFs of actual fabrics are lower than those of an ideal fabric. In most studies, thickness measurements for the fabrics were not undertaken or reported. However, thickness is a useful variable for understanding differences in UV protection between fabrics. It was reported that thicker, denser fabrics transmit less UV radiation and concluded that thickness is most useful in explaining differences in UV transmission when differences in percentage cover factor are also accounted for. [10&19]

2.14.3 Color and UV Absorbers

The dyes used to color a textile can affect the UV protectiveness of a fabric, depending on the position and intensity of the UV wavelength absorption bands of the dyes and the concentration of the dyes in the textile. The absorbance of UV radiation can affect substrate attributes, including fluorescence, photo degradation, and UV protection. Generally, dark colors provide better UV protection due to increased UV absorption.

However, particular hue dyes can vary considerably in the degree of UV protectiveness because of individual transmission and absorption characteristics. To improve UV protection, UV absorbers have been added using different techniques. Ultraviolet absorbers for laundry detergents and rinse cycle application have been recently developed. Ultraviolet absorbers are colorless compounds that absorb in the wavelength range of 290 to 400 nm. The cover factor is useful in predicting the maximum UPF achievable by treating yarns with UV absorbers. Thus, fabrics could be made opaque to UV radiation with a sufficient level of UV absorber impregnation, and the corresponding UPFs approached the theoretically predicted levels based on the cover factor. Titanium dioxide of various particle sizes is frequently used as a UV absorbing substance in fabrics; however, the absorption of these particles is frequently less protective in the UV-A wavelength range. Other manufactured UV absorbers also provide less protection from UV-A radiation, which should be considered when counseling patients with photosensitivity disorders. However, UV absorbers are suitable for enhancing UV protectiveness especially that of non-dyed lightweight summer fabrics, such as cotton and viscose, which offer a high level of wearing, comfort. [19]

2.15 Wearing conditions affecting UV protection of textiles

2.15.1 Stretch

Stretching a textile causes an increase in fabric porosity, with a consequent decrease in UPF. It that been found out that stretching elastane-based garments about 10% in the machine and cross-machine directions causes a dramatic decrease in the measured UPF of a textile. Textiles for tight fitting clothes should not be considered as UV protective clothing. It was reported that the UPF of 50-denier stockings decreased 868% when stretched 30% greater than their original size. Notably, the most popular type of stockings (15-denier) provides a UPF of less than two. The maximum stretch point on the body for tight fitting garments is the upper back, where textiles can be stretched up to 15%. However, realistically, the effect of stretch on the UPF of a textile may be significant only for garments with a non-stretched UPF of less than 30, particularly leggings, women's stockings, and swimsuits. [4, 8&19]

3 Methodology

3.1 Experimental Goal

The main goals of the experimental part was to observe the effect of different TiO_2 powders on textile material when using different treatment methods such as Sol-gel method, Print-paste method and the Hydrophobic treatment. The TiO_2 powder utilized during the experiment were labeled according to their trade names [091009/1, 181109/2, KAT 61 & KAT 66]. The other intended observations were to compare the wettability of the textiles materials before and after treatment, to measure the contact angle of the textile materials, and to determine the UPF (Ultraviolet protection factor) using the spectrophotometer.

3.1.1The material used for the experiment:

- Cotton
- Glass fiber
- Kevlar smooth surface
- Kevlar rough surface
- Polyester
- Wool

3.2 Description of the experimental processes

3.2.1 Dyeing of Cotton

The dyeing process was done on 100% cotton material with three different reactive dyes of low light fastness.

Characteristics of dyeing materials used;

- Liquor ratio 1:30

- 2% reactive dyes (C.I. REACTIVE ORANGE 4, C.I. REACTIVE RED 2 & C.I. REACTIVE BLUE 194)
- Sodium chloride salt, 40g/l
- Soda ash, 20g/l
- Syntapon ABA(anionic washing agent), 1-4g/

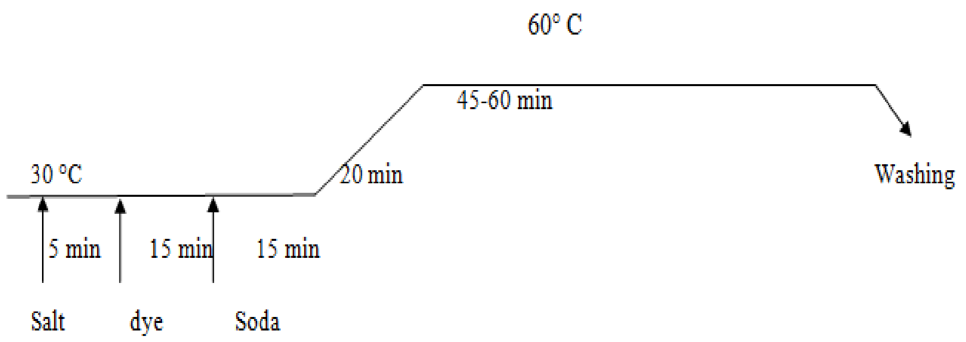


Figure 3 the diagram indicating the conditions of the dyeing process

3.2.2 The Print-Paste Method

The TiO_2 dispersions of different volumes were mixed with the white pigment paste, and the mixture was applied on different dyed cotton materials.

Procedure:

- 50g Pigment Paste
- TiO_2 volumes [0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4ml]
- Ultrasound machine used for stirring of mixture-1 minute, at speed 2000 rotation/min, AM (intensity)-10%, Energy- 0.398kj

3.2.3 The Sol-Gel Method

3.2.3.1 Preparation of sol based TMSPM

the basis for the preparation of sol was TMSPM ((3 -(trimethoxysilylpropylmethacrylate)

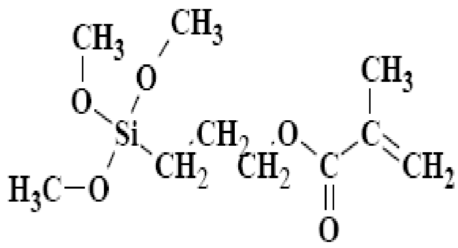


Figure 4: Chemical formula TMSPM

The principle of training consisted of sol dissolution TMSPM Mid required amount of IPA and the dissolution of other ingredients (water, HCl, BPO) in the second half of the required amount of IPA. Then the two solutions were mixed under vigorous stirring. Resulting sol was heated in boiling under reflux for 30 minutes after which the sol was cooled. Part of the final sol was diluted with IPA in the ratio 1:4. Sol was identified as AC4. Sol preparation made by Mgr.Veronika Zajícová at the Department of Chemistry TUL.

3.2.3.2 The application conditions of the sol gel with the TiO2 powder on 100% cotton fabric

- sol gel solution 20ml;
- TiO_2 weights 0.01g, 0.02g, 0.05g and 0.1g;
- Time of sample exposition to the sol gel/TiO_2 powder dispersion 1minute;
- drying at room temperature 20°C for 5 minutes
- The samples were then placed in a 85°C dryer for fixation process for 3 hours

Table 6 the weight of cotton sample before, after padding and after drying

Samples	Weight before padding (w_0) [g]	Weight after padding (w_w) [g]	Weight after drying (w_D) [g]
1	1.56996	2.44960	1.47449
2	1.52840	2.52034	1.52650
3	1.60499	2.62215	1.56241

Calculations:

Sample 1

- Percentage of liquor after padding [%] = $(w_w - w_0)/w_0 \times 100\%$

  = (2.44960g - 1.56996g)/1.5699g×100%

  = 56%

Sample 2

- Percentage of liquor after padding [%] = $(w_w - w_0)/w_0 \times 100\%$

  = (2.52034g -1.52840g)/1.52840g×100%

  = 60%

Sample 3

- Percentage of liquor after padding [%] = $(w_w - w_0)/w_0 \times 100\%$

  = (2.62215g - 1.60499g)/ 1.60499g × 100%

  = 63 %

- The average wet pick-up = (56+60+63)/3

  = 60%

3.2.3.3 Padding of samples on a Padder

Figure 5 Laboratory Padder Mathis HVF 69805

Machine parameters:

- Cylinder pressure – 0.6MPa
- Wet pick up – 60%
- Speed of cylinders 1mmin-1

3.2.4 Hydrophobic Treatment

The hydrophobic solution was prepared for the hydrophobic treatment of textiles. The application was done on 6 different fibres (Cotton, Glass, Kevlar-rough surface, Kevlar-smooth surface, Polyester and Wool).

Chemicals used for the preparation of the hydrophobic treatment solution

- 30g/l Lukofix T40D
- 20g/l Katalyzator C48

- 10ml/l Acetic acid (CH_3COOH)

Experimental procedure:

- About 30ml of the prepared hydrophobic treatment solution was mixed with different TiO_2 powders at various concentration : 0.1g/l, 0.5g/l, 1g/l, 5g/l, 10g/l, 20g/l
- The mixing of TiO_2 powder was done by the Ultrasound machine under the following settings; AM-30%, time- 2minutes, Energy -3.570KJ

3.2.4.1 The homogenization of TiO2 particles with Ultrasound machine

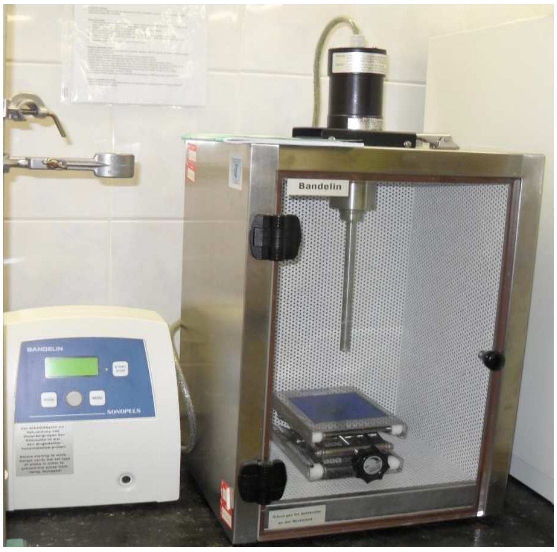


Figure 6 Laboratory Ultrasound machine

3.2.4.2 Drying and fixation of samples

The drying of samples was carried out immediately after padding at 90°C for 10 minutes for the hydrophobic treatment and fixation at 160°C for 3 minutes.

Figure 7 The Laboratory Drying machine

3.3 Methods of Analysis

3.3.1 Contact Angle Measuring Instrument

The contact angle was measured with a digital camera under the set light illumination. The settings below were used to measure the contact angle of all samples. The contact angle was measured with a 5µL pipette, and the water used was distilled.

Figure 8 the settings of the Contact angle measuring apparatus

3.3.2 Determination of contact angle values

The determination of contact angle values was done by imageJ software. ImageJ can display, edit, analyze, process, save, and print 8-bit, 16-bit and 32-bit images. It can read many image formats including TIFF, PNG, GIF, JPEG, BMP, DICOM, FITS, as well as raw formats. ImageJ supports image stacks, a series of images that share a single window, and it is multithreaded, so time-consuming operations can be performed in parallel on multi-CPU hardware. ImageJ can calculate area and pixel value statistics of user-defined selections and intensity threshold objects. It can measure distances and angles. It can create density histograms and line profile plots. It supports standard image processing functions such as logical and arithmetical operations between images, contrast manipulation, convolution, Fourier analysis, sharpening, smoothing, edge detection and median filtering. It does geometric transformations such as scaling, rotation and flips.

The program supports any number of images simultaneously, limited only by available memory. The image below is an example of a contact angle measured by the imageJ software to obtain the contact angle value.

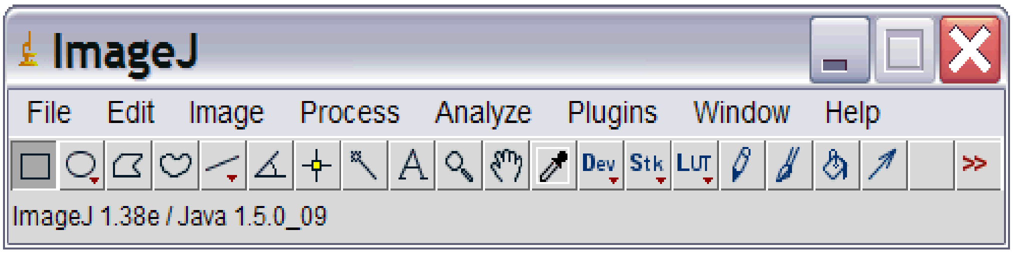


Figure 9 ImageJ software (Image processing and analysis in Java)

The figure below shows how the contact angle can be measured by the imageJ software.

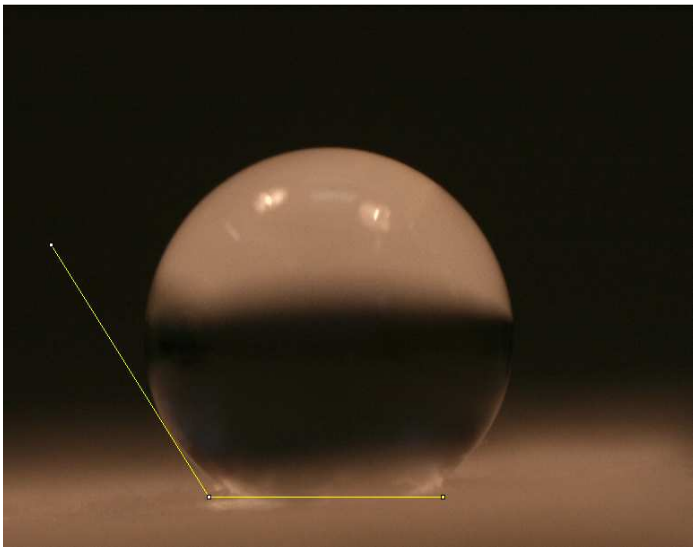


Figure 10. The measured droplet on hydrophobic treatment surface of polyester

3.3.3 Measuring of the UPF values

The UPF evaluates the reduction in the amount of the UV radiation that passes through the fabric to the skin. To determine the in vitro UPF, the spectral irradiance (of the source and transmitted spectrum) is weighted against the erythemal action spectrum, as follows

$$UPF = \frac{\int_{290}^{400} E_\lambda\, S_\lambda\, d_\lambda}{\int_{290}^{400} E_\lambda\, S_\lambda\, T_\lambda\, d_\lambda}$$

Where λ is the wavelength in nm; *S*, solar spectral irradiance of the source in watts per square meter; d, bandwidth in nanometer; and *T*-spectral transmission of the sample. The integrals (∫) are calculated over the wavelength range of 290 to 400 nm. *E*, relative erythemal spectral effectiveness. The used instrument for the measurement of UPF in this experiment was the

3.3.3.1 The parameters for the used Spectrophotometer

- Wavelength (nm) -290-400
- Scan speed- fast
- Type of instrument-UV-3100PC series
- Measuring mode-Transmittance
- Slid width-30
- Light source change wavelength (nm)-360

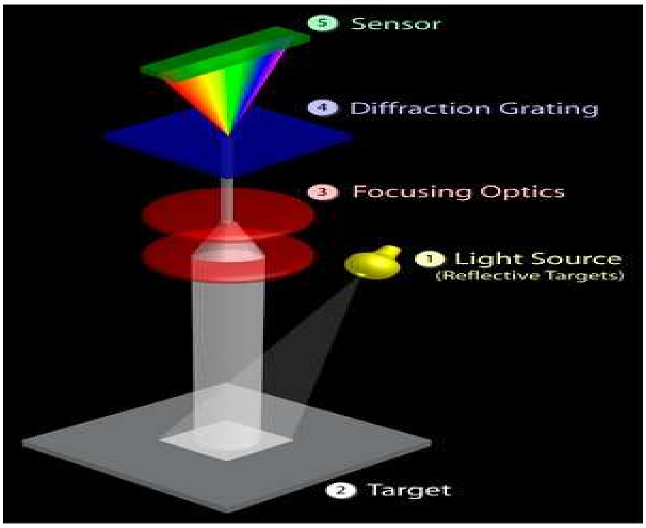


Figure 11 the general makeup of a spectrophotometer

3.3.4 Textile Image analysis for porosity measurement

For textile image analysis the following system was used; the Optical microscopy connected with computer which was also connected to camera with image analysis software.

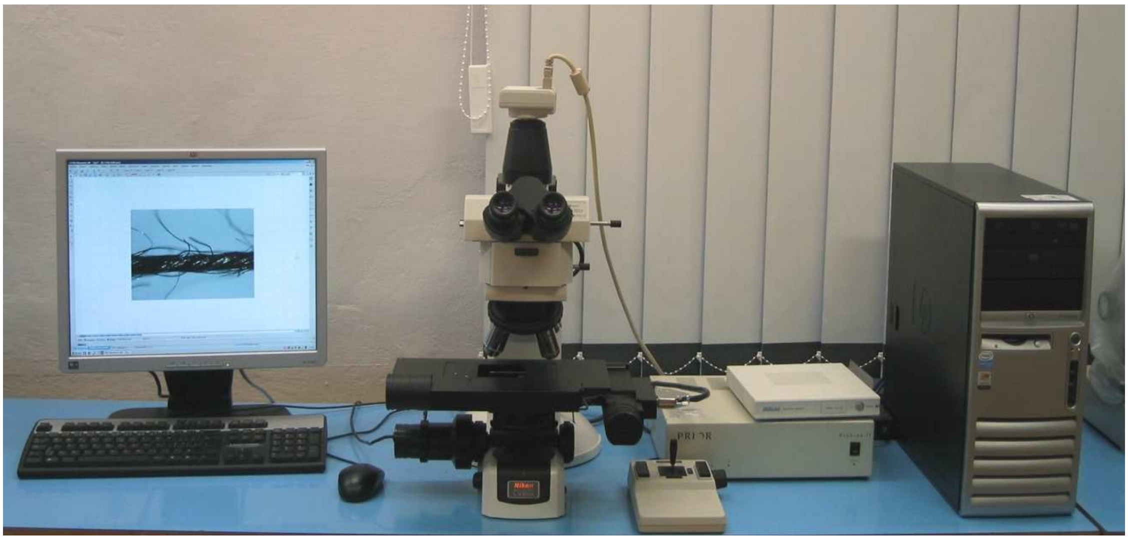


Figure 12 Image analysis system

5 Results

5.1 Results by printing technique

The results below show the relationship between UPF and TiO_2 concentration for cotton samples dyed with different reactive dyes.

Table 7 the results for UPF (Ultraviolet Protection Factor)

TiO_2/0.05kgPP	White Sample	Pink sample	Orange Sample	Blue sample
	UPF	UPF	UPF	UPF
0*	13	5195	2127	19321
0**	19	6345	2072	9677
0.5	86	64564	2283	19699
1	142	2358	11591	11278
1.5	210	10805	17953	37125
2	152	51164	19868	37125
2.5	277	81231	38114	7407
3	281	128112	45573	13236
3.5	311	377216	7697	37125
4	364	724022	364374	38837

NB: 0* - Untreated sample

0** - Dyed sample without TiO_2

PP-Pigment Paste

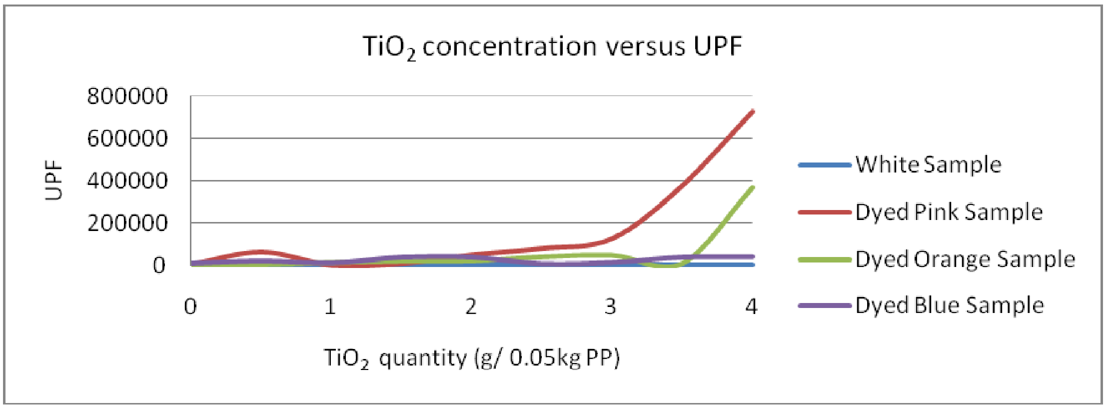


Figure 13 the relation between the UPF and the TiO_2 concentration

From the graph distribution above the results shows a low UPF value for cotton samples dyed with blue, white reactive dye and an increase of UPF for sample dyed with pink and orange reactive dyes as the TiO_2 concentration increases.

Table 8 Test for Cotton fabric Wettability

	White sample	Pink sample	Orange Sample	Blue Sample
TiO2 (g/ 0.05kg PP)	Time of absorption	Time of absorption	Time of absorption	Time of absorption
0*	0 sec	0 sec	0 sec	0 sec
0**	10 sec	1 sec	1 sec	0 sec
0.5	50 sec	2 sec	2 sec	1 sec
1	64 sec	2 sec	2 sec	1 sec
1.5	75 sec	2 sec	2 sec	1 sec
2	78sec	2 sec	2 sec	1 sec
2.5	89sec	2 sec	2 sec	2 sec
3	280 sec	2 sec	2 sec	2 sec
3.5	140 sec	2 sec	3 sec	3 sec
4	227 sec	5 sec	3 sec	3 sec

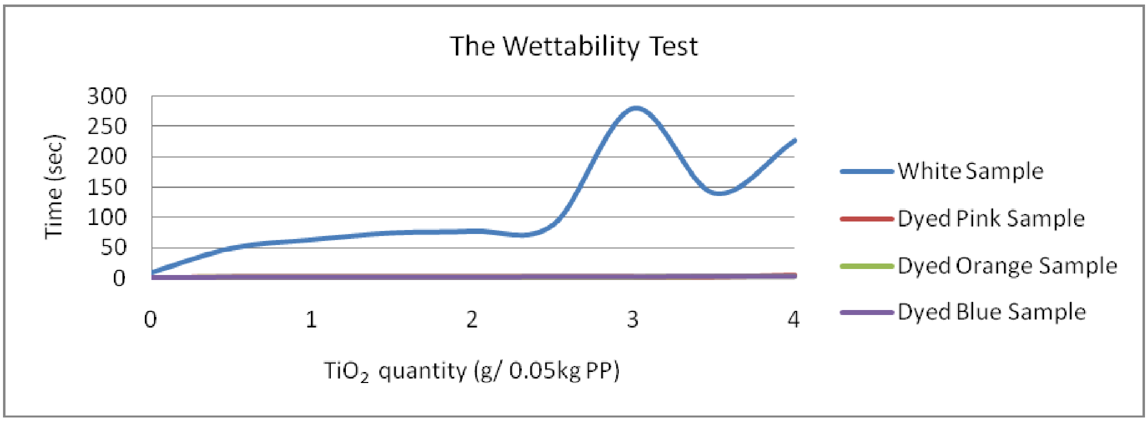


Figure 14 Comparison of the wettability of different dyed pigment paste printed samples

The wettability of cotton material was tested after printing with print paste-TiO_2 the figure above show the time it took for each sample to absorb water. The Dyed Pink, orange and blue samples absorbed water after a short period of time, whereas the white sample absorbed after a long period of time.

Table 9 TiO_2 concentration versus the lightness (L) of the color of the samples

	White Sample	Pink sample	Orange Sample	Blue sample
TiO_2 concentration (%)	Color lightness (L)	Color lightness (L)	Color lightness (L)	Color lightness (L)
0	93.34	49.49	64.04	32.0
0.5	93.40	48.64	64.08	35.8
1	93.01	49.06	64.74	37.0
1.5	93.20	49.60	65.48	35.0
2	93.47	49.13	64.85	36.0
2.5	93.63	48.82	66.53	33.0
3	93.53	49.47	65.68	37.4
3.5	93.67	48.39	65.86	36.9
4	93.72	49.82	65.88	34.45

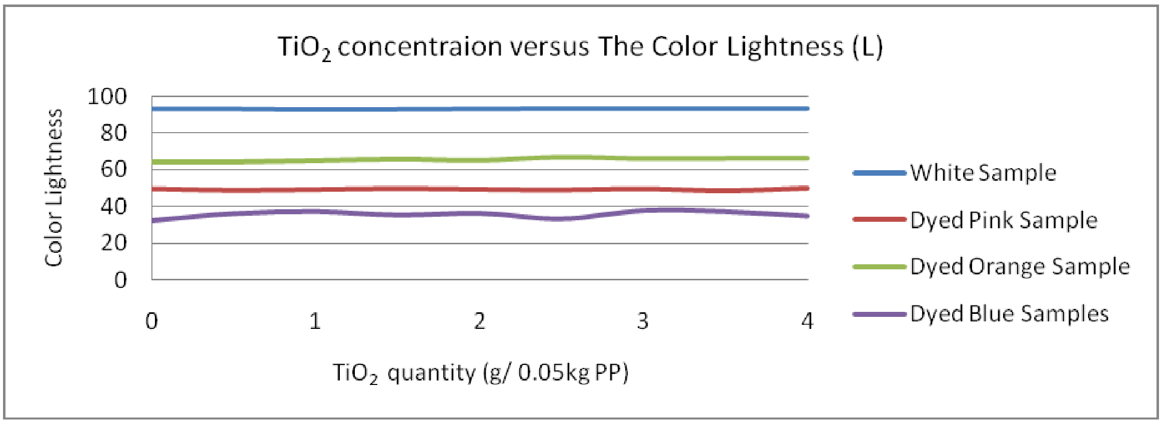


Figure 15 the color lightness in relation to the TiO_2 quantity

The color lightness is described as how dark or light the color is. In the results shown from the graph above, the TiO2 concentration is observed not to be having any effect on the color lightness of the sample, but the samples have different color lightness and the increasing order is as follows; blue lower , followed by pink, orange and then white sample as the highest L value.

5.2 Contact angle measurement results

5.2.1The Sol Gel method results

5.2.1.1 The Sol Gel treatment of Cotton with four different TiO2 powders

Table 10 Results for TiO_2 powder with trade name 091009/1

TiO_2 concentration (g/l)	Minimum value (X_{min})	The average Contact angle (θ°)	Maximum value (X_{max})
0	Unmeasurable	Unmeasurable	Unmeasurable
0.5	79.1	82.5	85.9
1.0	88.4	91.3	95.1
2.5	91.9	95.8	99.7
5.0	85.5	86.7	87.8

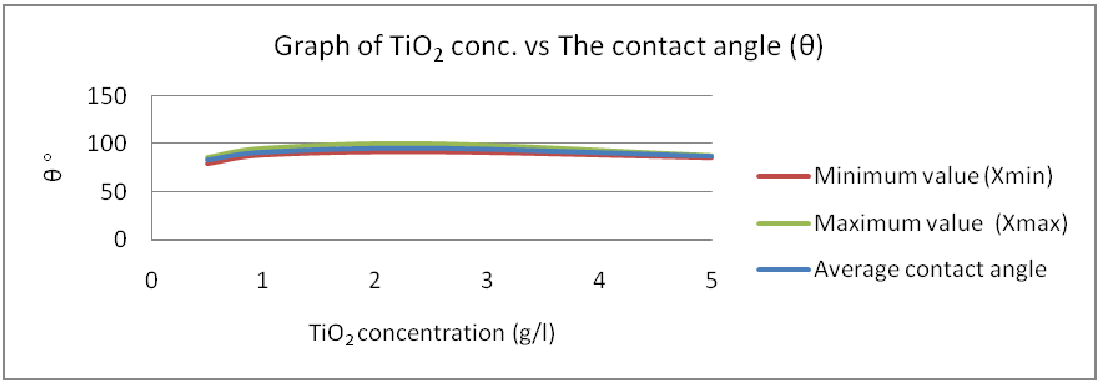


Figure 16 the graph showing the relation between the contact angle with sol-TiO_2 treated cotton surface for TiO_2-091009/1

The surface wettability was assessed by contact measured for sol-TiO_2 cotton treatment, showing the relationship between the sol-TiO_2 concentrations with the contact angle. In figure 5.2.1a the 0 concentration of the sol-TiO_2 on the cotton sample was not measurable due to the complete absorption of water by the cotton substrate. The graph distribution above shows the contact angle increasing at the low sol-TiO_2 concentration and decreasing towards the higher concentration

Table 11 Results for TiO_2 powder by trade name 181109/2

TiO_2 concentration (g/l)	Minimum value (X_{min})	Average contact angle (θ°)	Maximum value (X_{max})
0	Unmeasurable	Unmeasurable	Unmeasurable
0.5	104.54	106.61	108.69
1	103.14	105.03	106.92
2.5	104.92	106.71	108.50
5	102.21	103.87	105.52
10	102.63	103.46	104.29

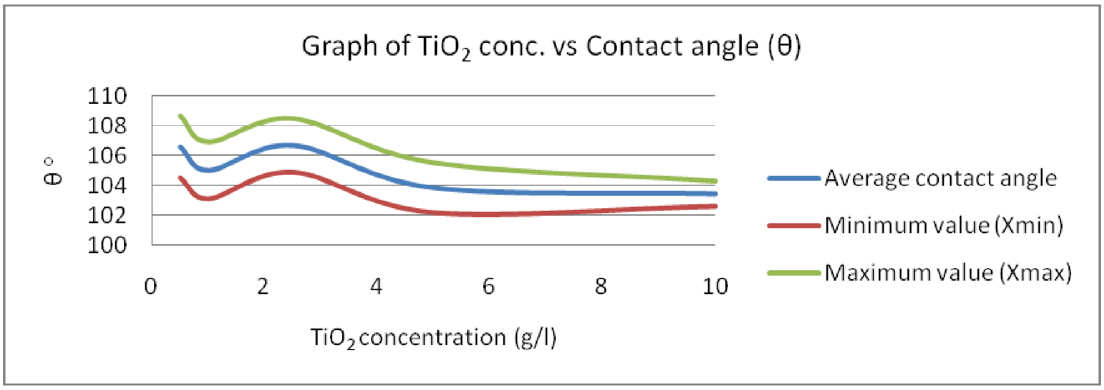


Figure 17 the graph showing the relation between the contact angle with sol-TiO_2 treated cotton surface for TiO_2-181109/2

With the use of TiO_2-181109/2 powder the contact angle distribution with the sol-TiO_2 concentration started with a decrease at 1g/l concentration, then an increase at 2.5g/l concentration and further decline to a constant distribution till high concentration.

Table 12 Results for TiO_2 powder with trade name KATI 61

TiO_2 (g/l)	Minimum value	Average Contact angle	Maximum value (X_{max})
0	Unmeasurable	Unmeasurable	Unmeasurable
0.5	101.15	102.08	103.02
1.0	101.59	102.27	102.95
2.5	92.75	94.92	97.09718
5.0	99.83	101.32	102.80
10.	103.39	105.06	106.74

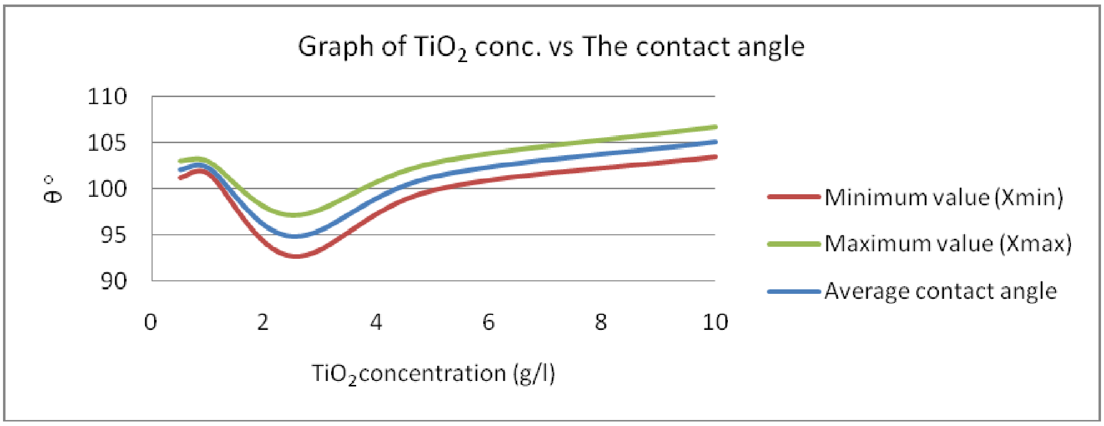


Figure 18 the graph of contacts angle with sol-TiO_2 treated cotton surface for TiO2-KATI61

The TiO_2-KATI61 is showing a contact angle distribution whereby at concentration 2.5g/l is decreasing with the sol-TiO_2 concentration, and further increasing as the concentration increases.

Table 13 Results for TiO_2 powder with trade name KATI 66

TiO_2 concentration (g/l)	Minimum value (X_{min})	Average Contact angle (θ°)	Maximum value (X_{max})
0	Unmeasurable	Unmeasurable	Unmeasurable
0.5	110.01	113.16	116.30
1	105.42	106.76	108.10
2.5	103.78	104.72	105.67
5	103.17	104.77	106.38
10	102.40	104.58	106.75

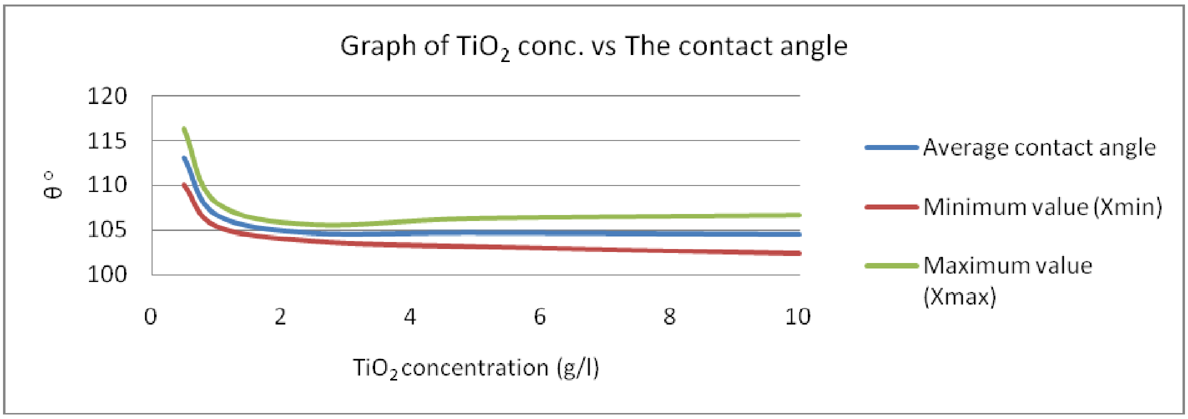


Figure 19 the graph of contact angles with sol-TiO_2 concentration on treated cotton surface for TiO2- KATI 66

The figure above shows that the contact angle is increasing at low concentration and further decreases at high concentration. But from the sol-TiO_2 of 5g/l the distribution is constant, that is the contact angle is more or less the same.

5.2.2 Hydrophobic Treatment Results

5.2.2.1 Hydrophobic Treatment of Cotton with different TiO_2 powders

Table 14 Results for TiO_2 powder with trade name 091009/1

TiO_2 concentration (g/l)	Minimum value (X_{min})	Average Contact angle (θ°)	Maximum value (X_{max})
0	95.40	96.90	98.40
0.1	103.17	105.21	107.24
0.5	101.87	103.65	105.44
1.0	102.41	103.61	104.80
5.0	102.77	104.64	106.51
10.	104.89	106.55	108.22
20	102.71	104.29	105.87

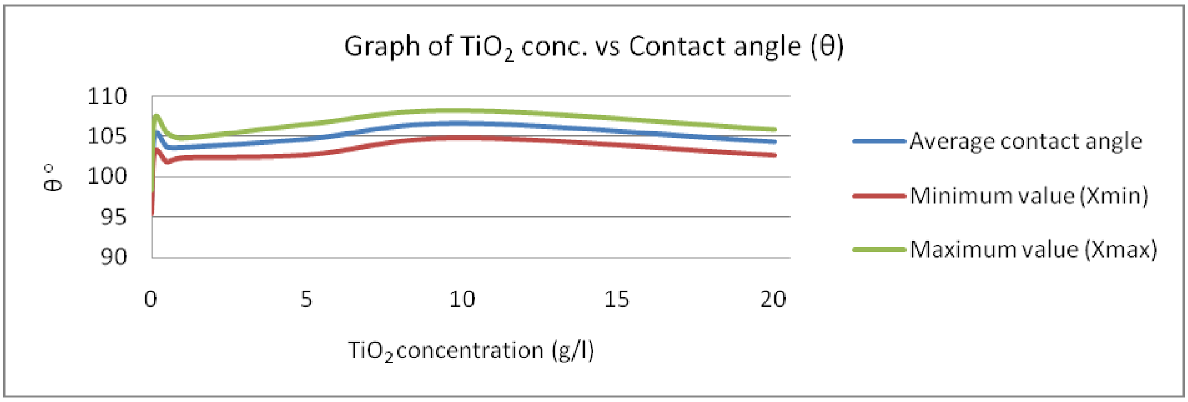


Figure 20 The graph of contact angle with hydrophobic-TiO_2 treated cotton surface for TiO2-091009/1

The figure above shows the graph distribution of the contact angle,in which the wettability of the cotton surface is assessed on the hydrophobic-TiO_2 treated cotton surface. The TiO_2-091009/1 powder in hydrophobic treatment shows the contact angle increasing from the low TiO_2 concetration and to the maximum increase at 10g/l,then a decrease as the concentration decreases.

Table 15 Results for TiO_2 powder with trade name 81109/2

TiO_2 concentration (g/l)	Minimum value (X_{min})	Average Contact angle (θ°)	Maximum value (X_{max})
0	95.40	96.90	104.71
0.1	102.43	103.57	103.37
0.5	100.40	101.89	104.55
1.0	101.70	103.12	108.15
5.0	102.95	105.55	105.06
10.	103.27	104.16	104.13
20	102.59	103.36	104.72

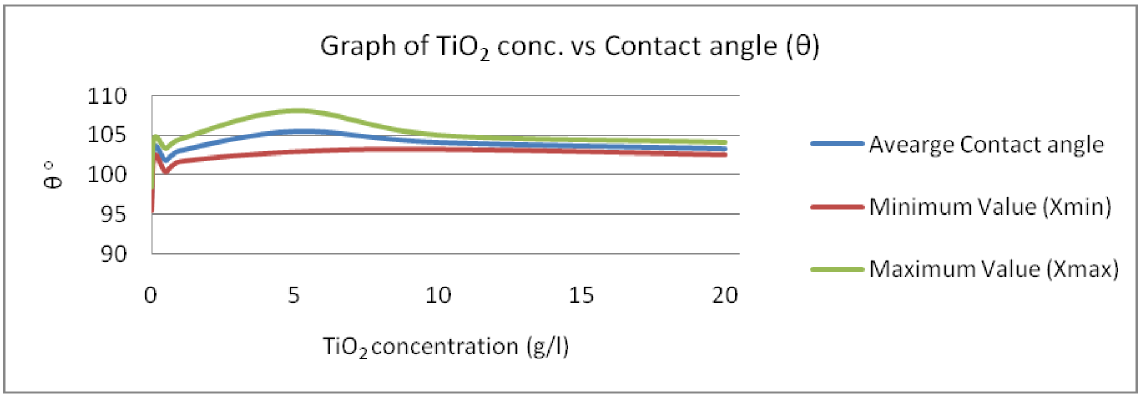


Figure 21 the graph of contact angle with hydrophobic -TiO_2 treated cotton surface for TiO2-81109/2

For the distribution in fig21 the contact angle is showing its maximum distibution at concentration of 5g/l and the decrease to a constant distribution as the concentration increases.That is the contact angle is more or less the same for the concentartion of TiO_2 from 10g/l to 20g/l.

Table 16 Results for TiO_2 powder with trade name KATI 61

TiO_2 concentration (g/l)	Minimum value (X_{min})	Average Contact angle (θ°)	Maximum value (X_{max})
0	95.37	96.90	98.43
0.1	102.39	103.85	105.30
0.5	102.42	103.93	105.44
1.0	102.86	104.17	105.49
5.0	104.04	106.26	108.48
10.	104.79	106.25	107.71
20	104.92	106.32	107.72

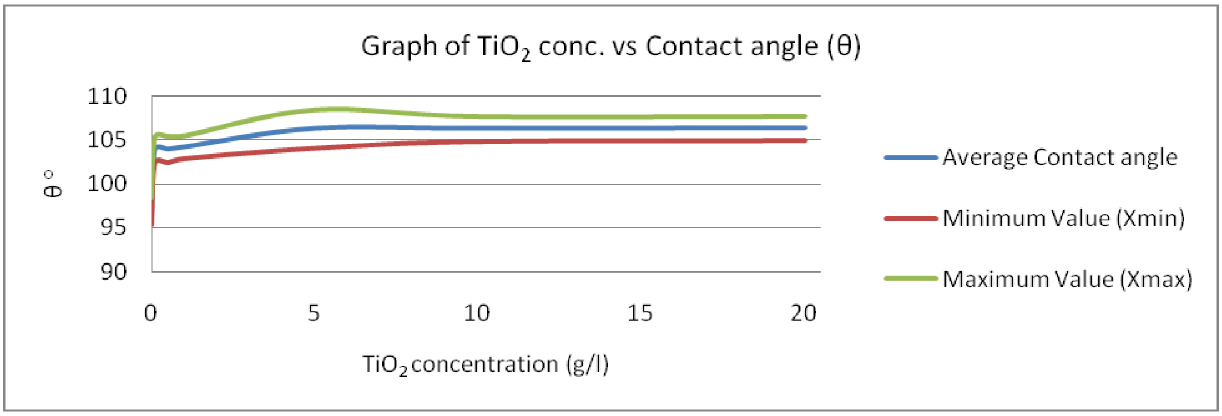


Figure 22 the graph of contact angle with hydrophobic-TiO_2 treated cotton surface for TiO_2 -KATI 61

For the distribution if fig22 the contact angle is showing its maximum distibution at concentration of 5g/l and the decrease to a constant distribution as the concentration increases.The contact angle at fig21 has more or less the same contact angle distribution as in fig 20.

Table 17 Results for TiO_2 powder with trade name KATI 66

TiO_2 concentration (g/l)	Minimum value (X_{min})	Average Contact angle (θ°)	Maximum value (X_{max})
0	95.37	96.90	98.43
0.1	104.72	106.41	108.11
0.5	106.62	107.99	109.35
1.0	105.79	106.56	107.33
5.0	105.96	107.58	109.21
10.	106.31	107.21	108.12
20	106.93	108.22	109.50

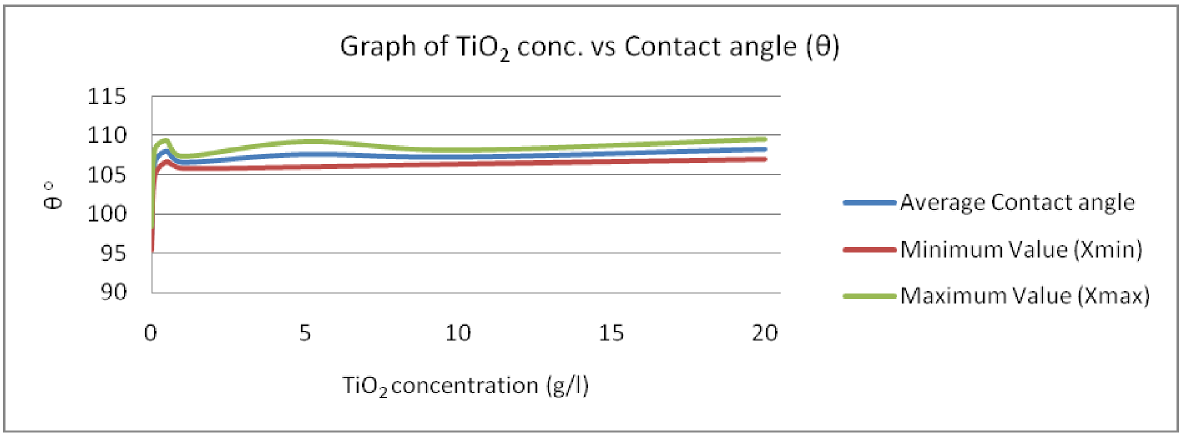


Figure 23 Description of the relation between the Contact angle and TiO_2 concentration for TiO_2- KATI 66

The graph above shows the contact angle increasing with increasing concentration. At concentration 5g/l the contact angle has the maximum value and from the 10-20g/l concentration the concentration is constant.

5.2.2.2 Hydrophobic Treatment of Glass Fibers with different TiO_2 powders

Table 18 Results for TiO_2 powder with trade name 091009/1

TiO_2 concentration (g/l)	Minimum value (X_{min})	Average Contact angle (θ°)	Maximum value (X_{max})
0	97.24	98.50	99.75
0.1	107.16	108.72	110.28
0.5	103.95	105.92	107.89
1.0	104.59	106.32	108.04
5.0	102.03	104.09	106.14
10.	102.86	105.37	107.89
20	104.99	107.14	109.28

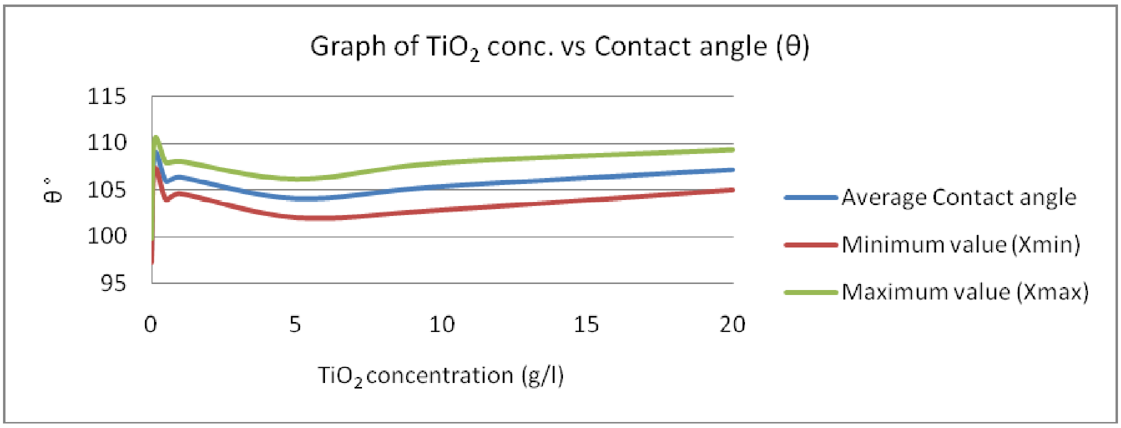


Figure 24 Description of the relation between the Contact angle and TiO_2 concentration for TiO2-091009/1

In the results above the contact angle is high at 0.1g/l concentration and then decreases at 5g/l concentration. As it moves further to the increasing concentration the contact angle is constant.

Table 19 Results for TiO_2 powder with trade name 81109/2

TiO_2 concentration (g/l)	Minimum value (X_{min})	Average Contact angle (θ°)	Maximum value (X_{max})
0	97.17	98.50	99.82
0.1	100.31	102.57	104.83
0.5	104.54	105.29	106.03
1.0	101.79	104.47	107.14
5.0	103.01	104.51	106.01
10.	101.99	103.43	104.85
20	101.69	104.14	106.59

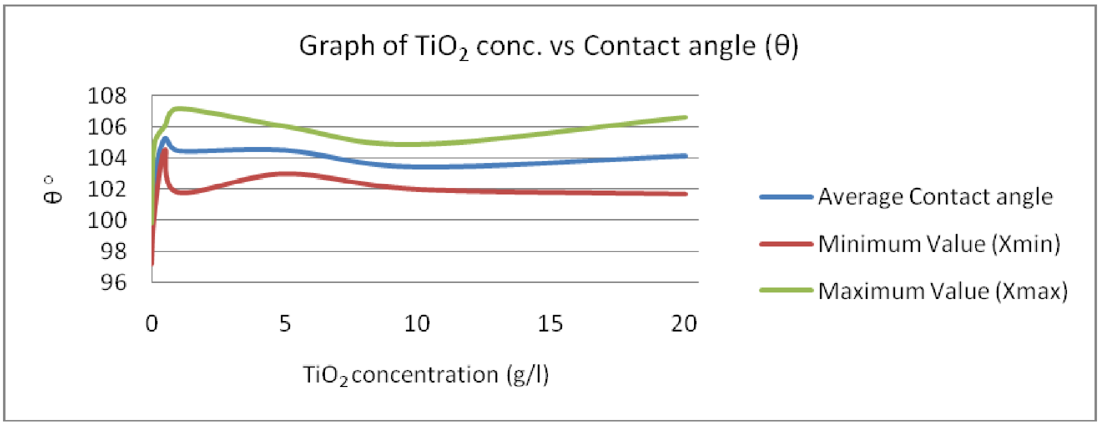


Figure 25 Description of the relation between the Contact angle and TiO_2 concentration for TiO_2-81109/2

The finishing treatment by the use of the TiO_2 -81109/2 the highest contact angle value at concentration 1g/l and the a decrease towards concentration 5g/l.and then a little bit of an increase but still less that at concentration 1g/l.

Table 20 Results for TiO_2 powder with trade name KATI 61

TiO_2 concentration (g/l)	Minimum value (X_{min})	Average Contact angle (θ°)	Maximum value (X_{max})
0	97.380	98.50	99.62
0.1	104.03	105.05	106.07
0.5	102.90	104.13	105.35
1.0	103.69	104.47	105.25
5.0	103.73	104.48	105.24
10.	103.69	104.45	105.21
20	104.98	106.01	107.04

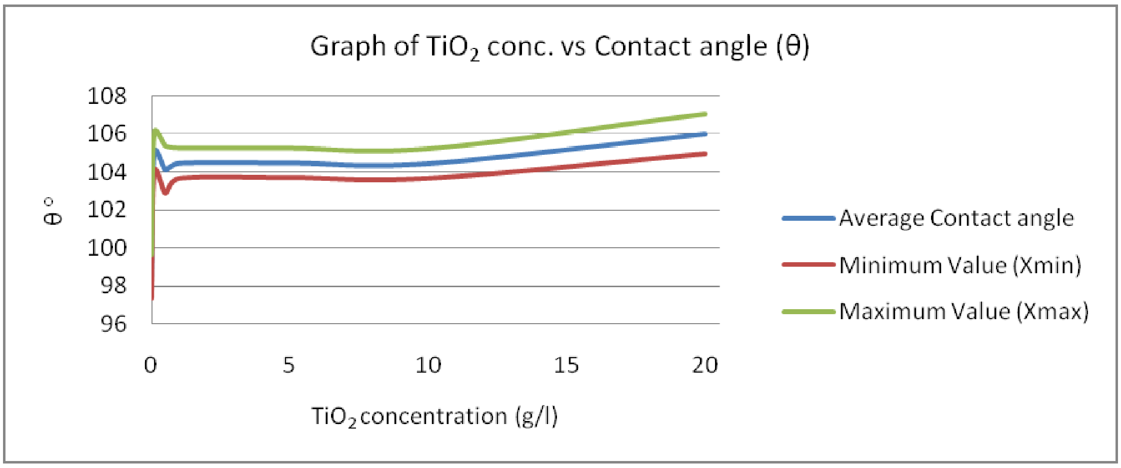


Figure 26 Description of the relation between the Contact angle and TiO_2 concentration

The presence of TiO_2-KATI has the same effect as in fig 25 in terms of a high increase at 1g/l concentration. The graph becomes constant between 5-10g/l and then increases as the concentration increases.

Table 21 Results for TiO_2 powder with trade name KATI 66

TiO_2 concentration (g/l)	Minimum value (X_{min})	Average Contact angle (θ°)	Maximum value (X_{max})
0	97.38	98.50	99.62
0.1	101.35	102.17	102.98
0.5	103.84	105.60	107.36
1.0	105.19	106.41	107.63
5.0	107.46	108.11	108.77
10.	105.83	106.70	107.56
20	106.36	107.28	108.20

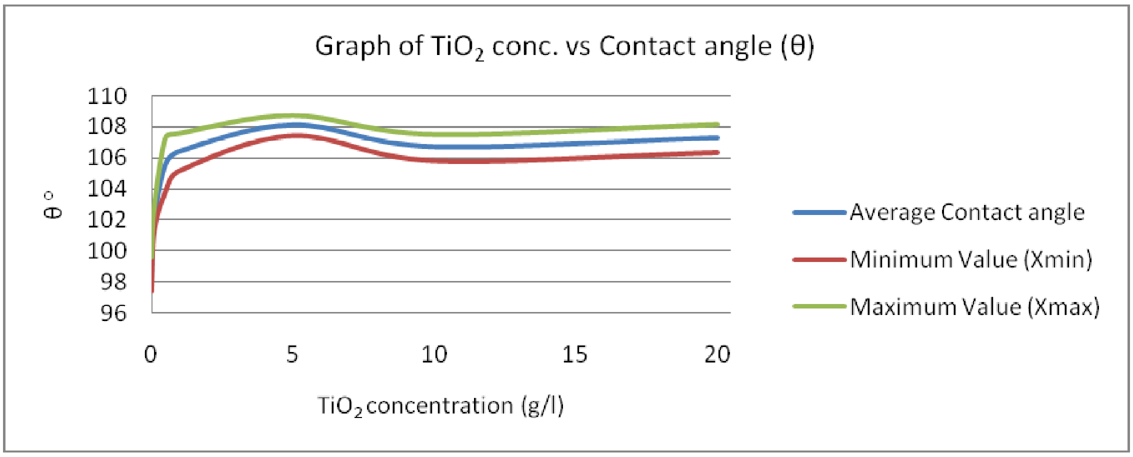


Figure 27 Description of the relation between the Contact angle and TiO_2 concentration

A different observation is obtained at KATI66 concentration as compared to fig 25 and fig26,not much difference, the graph still possess the same property og increasing with increasing concentration. The highest contact angle in fig27 at 5g/l concentration and the a constant distribution followed buy a little increase.

5.2.2.3 Hydrophobic Treatment of Kevlar-rough surface with different TiO_2 powders

Table 22 Results for TiO_2 powder with trade name 091009/1

TiO_2 concentration (g/l)	Minimum value (X_{min})	Average Contact angle (θ°)	Maximum value (X_{max})
0	97.78	98.95	100.11
0.1	98.63	100.64	102.64
0.5	103.56	105.61	107.67
1.0	105.09	107.32	109.55
5.0	105.01	107.12	109.22
10.	105.26	107.11	108.97
20	105.26	106.82	108.39

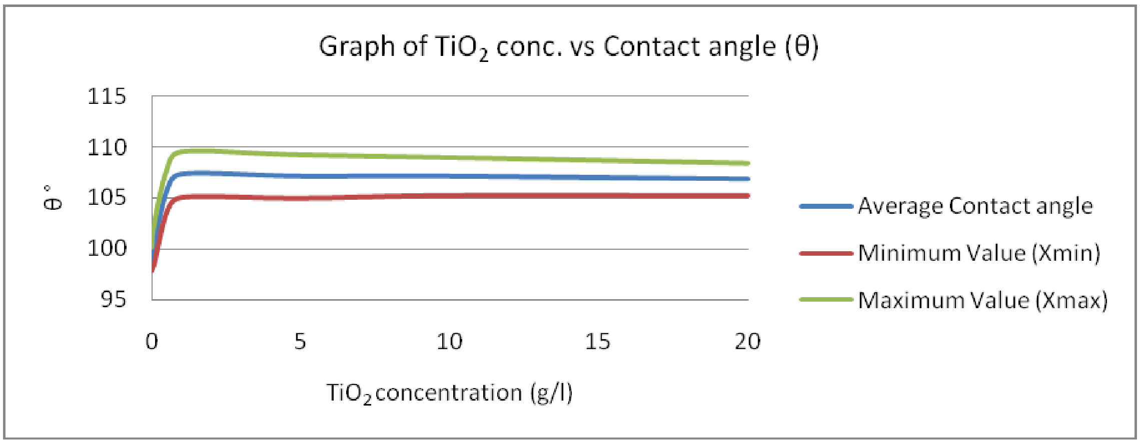


Figure 28 Description of the relation between the Contact angle and TiO_2 concentration

In the fig above a high contact angle value is observed at 1g/l concentration and then a constant contact angle from the 5g/l to20g/l. more of less the same properties are observed as in the previous figures.

Table 23 Results for TiO_2 powder with trade name 81109/2

TiO_2 concentration (g/l)	Minimum value (X_{min})	Average Contact angle (θ°)	Maximum value (X_{max})
0	97.71	98.95	100.19
0.1	104.75	105.64	106.53
0.5	104.24	105.62	106.99
1.0	104.48	105.93	107.38
5.0	102.67	104.02	105.38
10.	101.77	103.19	104.60
20	101.86	103.09	104.32

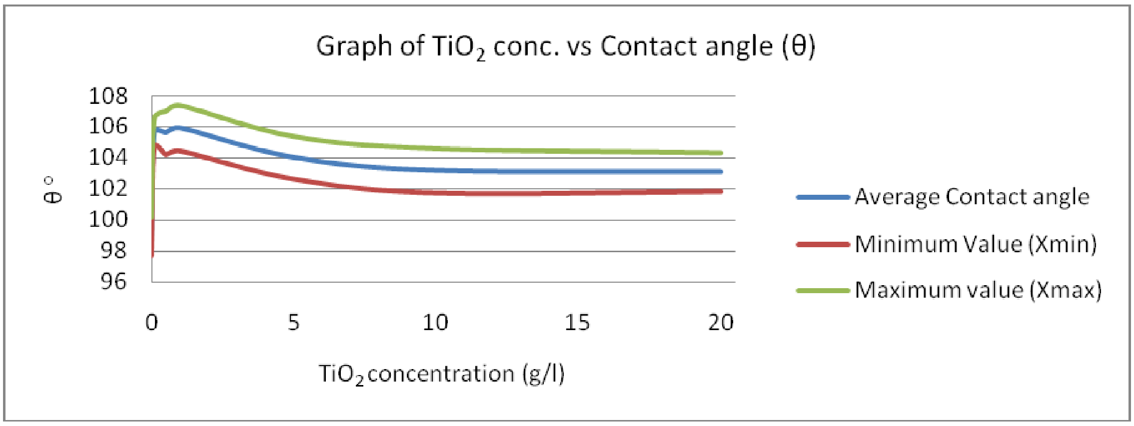


Figure 29 Description of the relation between the Contact angle and TiO2 concentration

The graph possesses same properties as fig28, an increase as concentration increases, and then a constant distribution.

Table 24 Results for TiO_2 powder with trade name KATI 61

TiO_2 concentration (g/l)	Minimum value (X_{min})	Average Contact angle (θ°)	Maximum value (X_{max})
0	97.71	98.95	100.19
0.1	99.83	101.08	102.32
0.5	101.40	102.51	103.62
1.0	101.63	102.91	104.18
5.0	101.89	103.34	104.80
10.	102.39	103.16	103.93
20	107.28	106.36	108.2

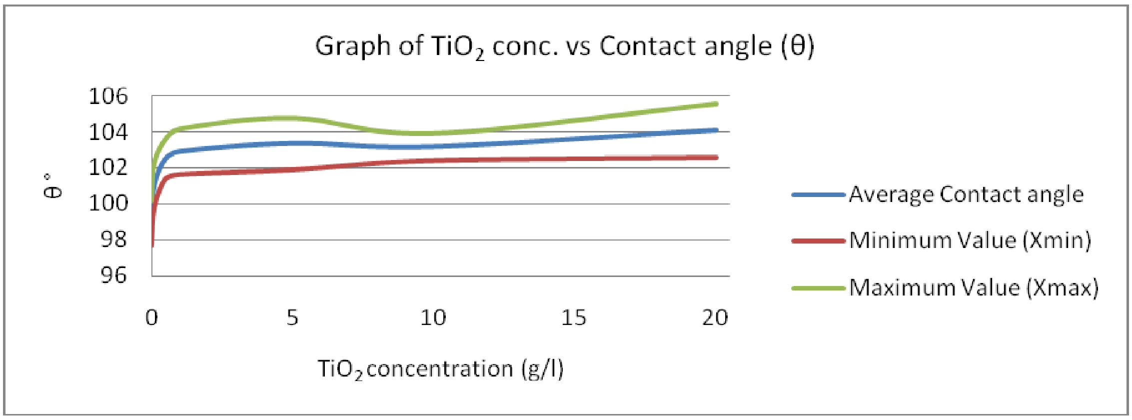


Figure 30 Description of the relation between the Contact angle and TiO_2 concentration

In the graph above the highest contact angel value was observed at concentration 20g/l, that is an increase from low concentration w as observed.

Table 25 Results for TiO_2 powder with trade name KATI 66

TiO_2 concentration (g/l)	Minimum value (X_{min})	Average Contact angle (θ°)	Maximum value (X_{max})
0	97.71	98.95	100.19
0.1	103.65	104.88	106.11
0.5	102.13	103.60	105.06
1.0	103.95	105.78	107.62
5.0	102.67	104.73	106.79
10.	104.16	105.0	105.77
20	105.89	107.14	108.38

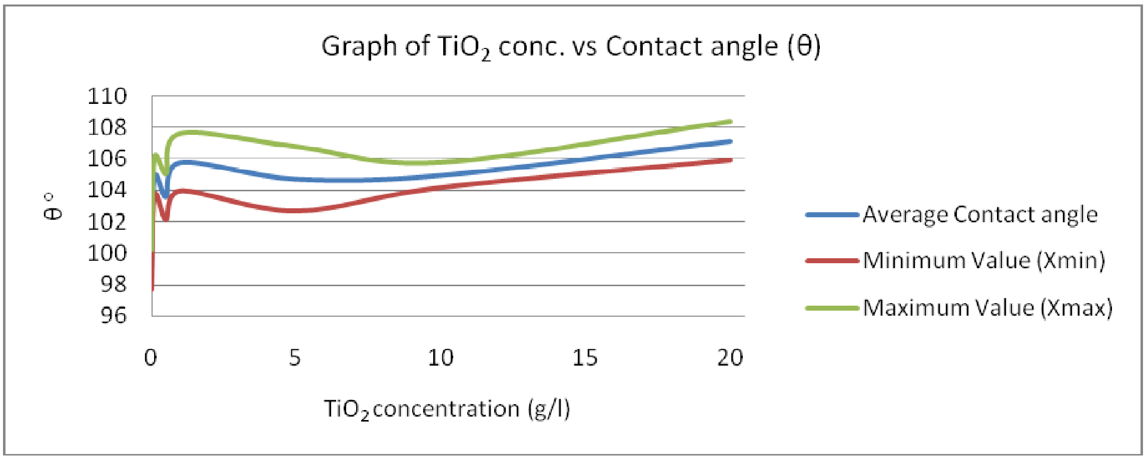


Figure 31Description of the relation between the Contact angle and TiO_2 concentration

The same observations as fig30, the highest contact angle value at concentration 20g/l.

Table 26 Results for TiO_2 powder with trade name 81109/2

TiO_2 concentration (g/l)	Minimum value (X_{min})	Average Contact angle (θ°)	Maximum value (X_{max})
0	95.69	96.61	97.53
0.1	100.54	102.17	103.79
0.5	101.47	102.96	104.45
1.0	102.44	103.64	104.84
5.0	102.21	103.55	104.89
10.	101.04	102.56	104.09
20	101.93	103.78	105.63

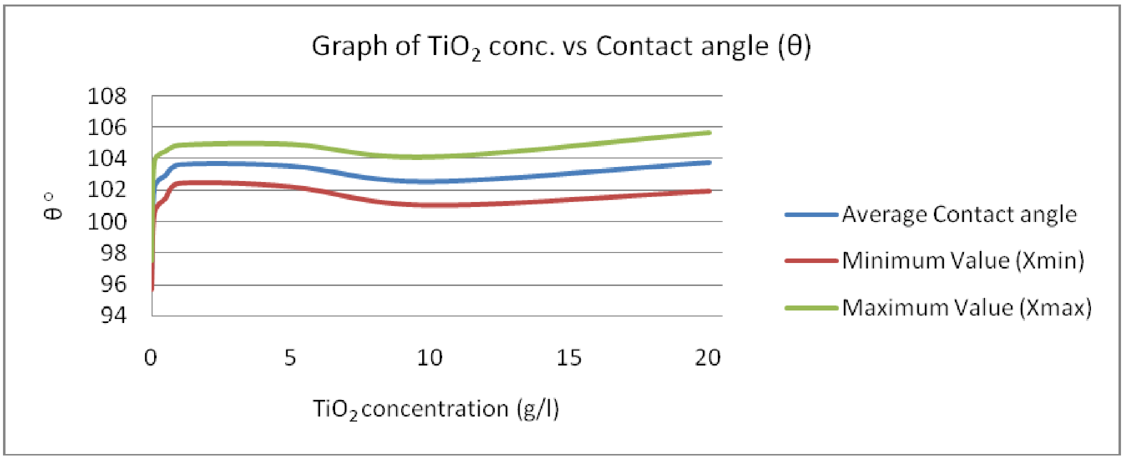


Figure 32 Description of the relation between the Contact angle and TiO_2 concentration

In this fig above same observation as in fig 30 and fig31; the contact angle increases with increasing TiO2 concentration.

Table 27 Results for TiO_2 powder by trade name KATI 61

TiO_2 concentration (g/l)	Minimum value (X_{min})	Average Contact angle (θ°)	Maximum value (X_{max})
0	95.69	96.61	97.52
0.1	98.75	100.87	102.99
0.5	100.56	101.49	102.42
1.0	97.89	99.51	101.13
5.0	100.72	101.82	102.92
10.	101.17	102.08	102.99
20	99.21	101.08	102.94

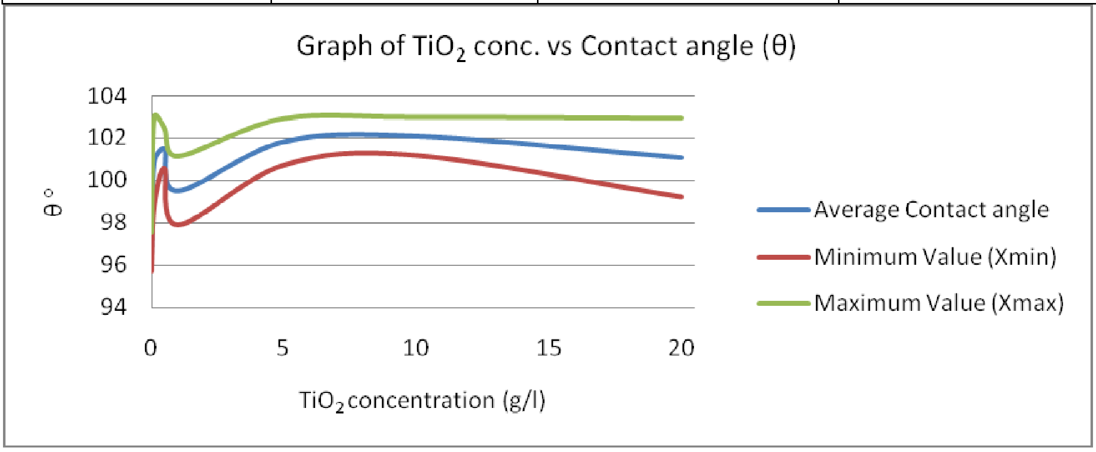


Figure 33 Description of the relation between the Contact angle and TiO_2 concentration

The graph shows an increase at the 0.5g/l,followed by a tremendous decrease at 1g/l concentration, and then a increase is observed for a while followed by a slightly decrease towards the high concentration. The graph was showing an increasing as in all cases but the contatct angle was variaying as the concentration increases. Nevertheless same properties as in other graphs was observed.

Table 28 Results for TiO_2 powder by the trade name KATI 66

TiO_2 concentration (g/l)	Minimum value (X_{min})	Average Contact angle (θ°)	Maximum value (X_{max})
0	95.69	96.61	97.52
0.1	101.60	103.33	105.07
0.5	98.70	100.24	101.78
1.0	100.65	101.93	103.20
5.0	99.71	100.64	101.56
10.	100.87	102.22	103.56
20	100.71	102.09	103.46

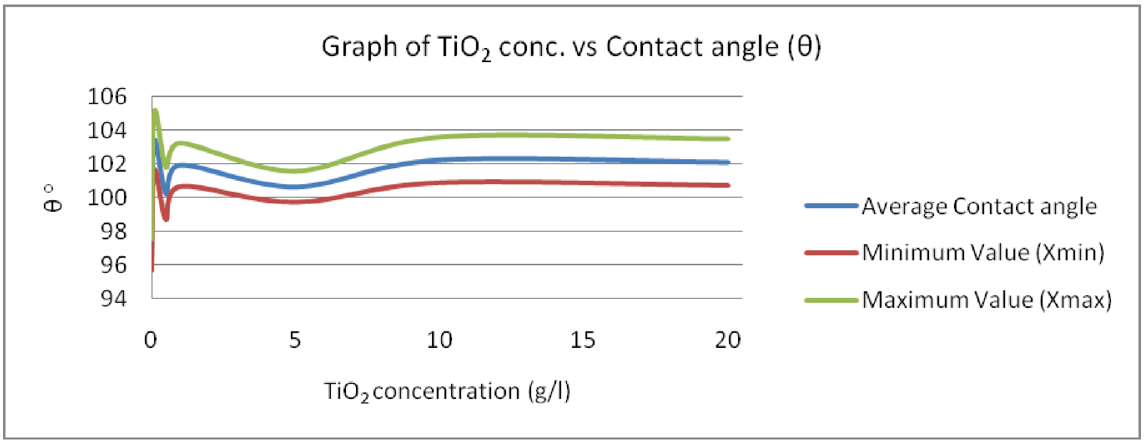


Figure 34 Description of the relation between the Contact angle and TiO_2 concentration

The same properties are observed as in fig33, only difference is the increasing after the 5g/l concentration towards the highest concentration, and the highest contact was observed at this high concentration.

5.2.2.4 Hydrophobic Treatment of Polyester with four different TiO2 powder

Table 29 Results for TiO_2 powder with trade name 091009/1

TiO_2 concentration (g/l)	Minimum value (X_{min})	Average Contact angle (θ°)	Maximum value (X_{max})
0	97.90	98.85	99.80
0.1	105.93	107.09	108.25
0.5	102.99	104.47	105.94
1.0	103.35	104.67	105.99
5.0	102.92	103.84	104.76
10.	103.10	104.89	106.67
20	103.15	104.29	105.42

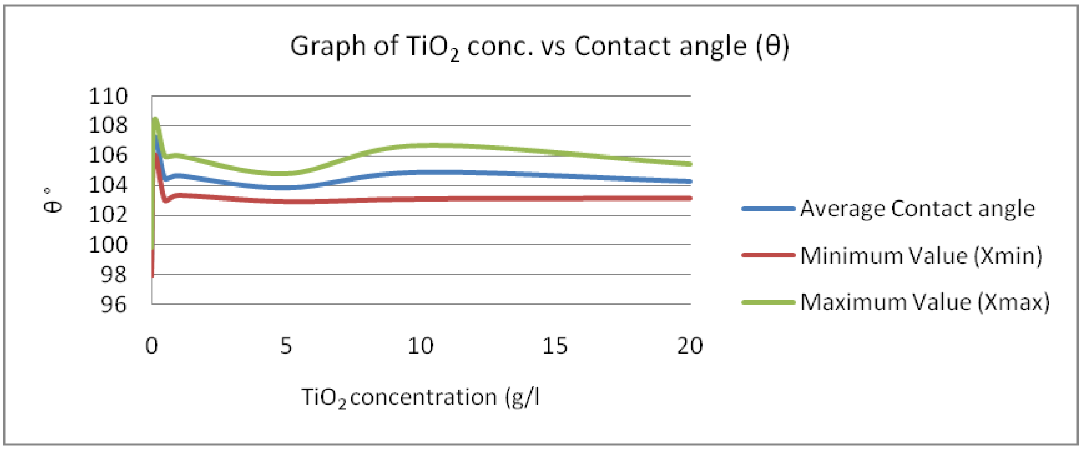


Figure 35 Description of the relation between the Contact angle and TiO_2 concentration

As with other graphs the same increasing properties as the concentration increases is also observed. Same property as in fig34.

Table 30 Results for TiO_2 powder with trade name 81109/2

TiO_2 concentration (g/l)	Minimum value (X_{min})	Average Contact angle (θ°)	Maximum value (X_{max})
0	97.49	98.85	100.21
0.1	102.35	103.86	105.36
0.5	103.46	104.28	105.10
1.0	102.69	103.71	104.73
5.0	104.40	105.69	106.97
10.	103.42	104.57	105.72
20	103.74	105.73	107.72

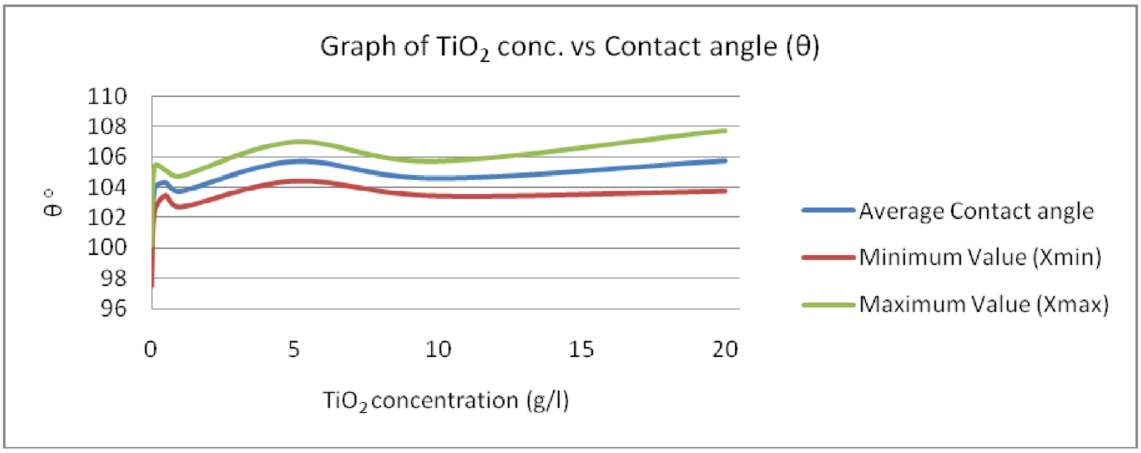


Figure 36Description of the relation between the Contact angle and TiO_2 concentration

As it cannot become as a surprise because as we were progressing with the discussing the only property that the graphs have in common is the increasing tendency as the TiO2 concentration increases and the same observations obtained in fig36.

Table 31 Results for TiO_2 powder with trade name KATI 61

TiO_2 concentration (g/l)	Minimum value (X_{min})	Average Contact angle (θ°)	Maximum value (X_{max})
0	97.58	98.85	100.13
0.1	100.82	102.14	103.46
0.5	100.61	101.81	103.00
1.0	100.15	101.11	102.06
5.0	100.69	101.57	102.45
10.	102.29	103.68	105.07
20	101.91	103.56	105.201

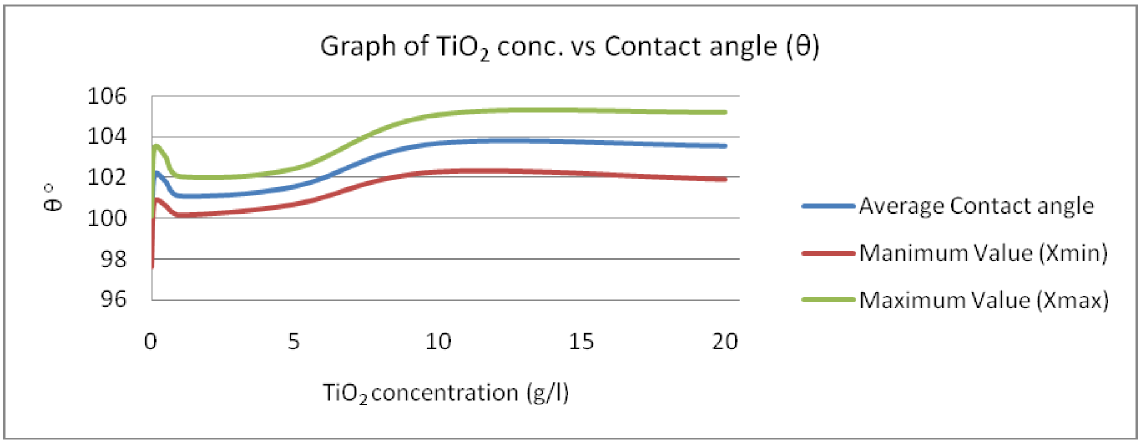


Figure 37 Description of the relation between the Contact angle and TiO_2 concentration

An increase as the concentration increase is also observed and the highest contact angle that can be useful is observed at concentration 10g/l.

Table 32 Results for TiO_2 powder with trade name KATI 66

TiO_2 concentration (g/l)	Minimum value (X_{min})	Average Contact angle (θ°)	Maximum value (X_{max})
0	97.58	98.85	100.13
0.1	103.99	105.37	106.74
0.5	104.99	105.70	106.39
1.0	104.11	105.68	107.25
5.0	103.54	104.55	105.66
10.	104.09	105.27	106.46
20	105.02	106.45	107.88

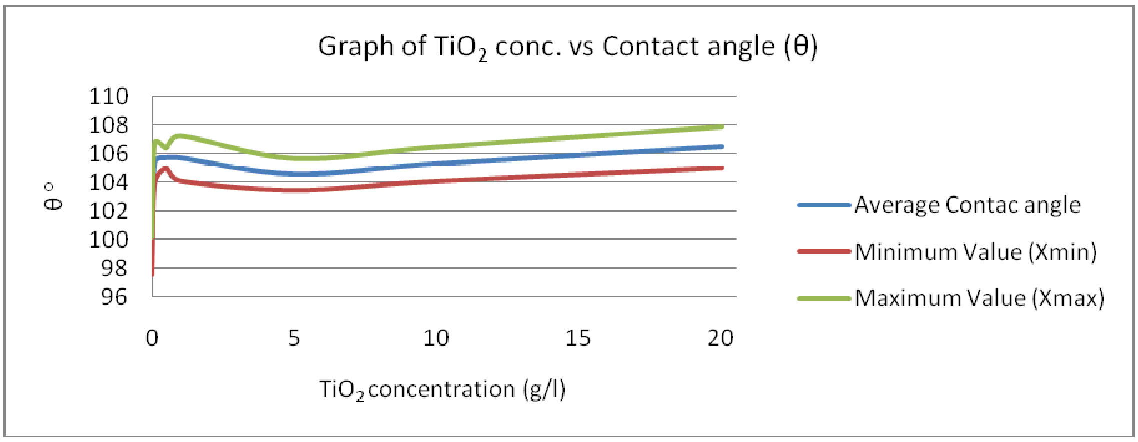


Figure 38 Description of the relation between the Contact angle and TiO_2 concentration

Same increasing tendency is observed as in other graphs and in this graph the highest useful contact angle is at 20g/l TiO2 concentration.

5.2.2.5 Hydrophobic Treatment of Wool with different TiO_2 powders

Table 33 Results for TiO_2 powder with trade name 091009/1

TiO_2 concentration (g/l)	Minimum value (X_{min})	Average Contact angle (θ°)	Maximum value (X_{max})
0	97.45	98.54	99.63
0.1	106.40	107.57	108.73
0.5	104.69	106.11	107.53
1.0	104.46	106.80	109.15
5.0	106.23	108.05	109.88
10.	103.76	105.71	107.67
20	102.68	104.09	105.51

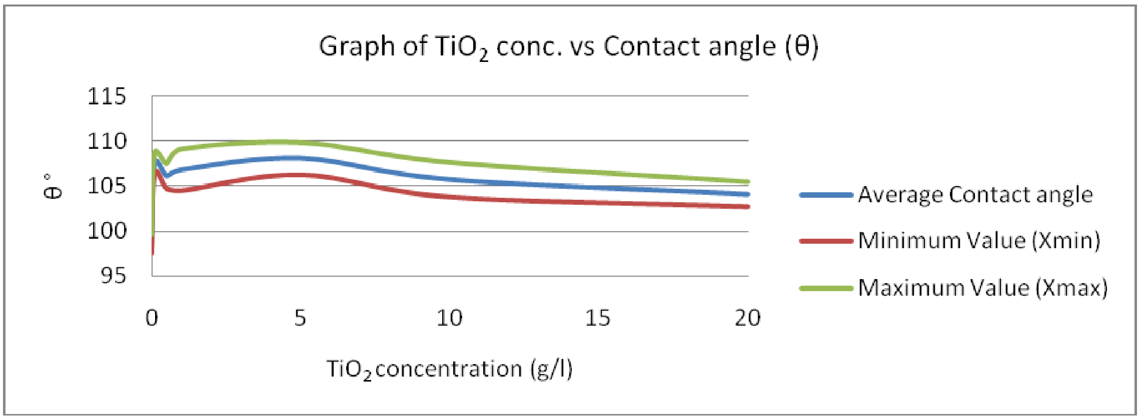


Figure 39 Description of the relation between the Contact angle and TiO_2 concentration

In the treatment of wool sample with this TiO2- 091009/1, the useful contact value is observed at concentration 5g/l as it was the highest and a decrease in contact angle is observed as the concentration increases.

Table 34 Results for TiO_2 powder with trade name 81109/2

TiO_2 concentration (g/l)	Minimum value (X_{min})	Average Contact angle (θ°)	Maximum value (X_{max})
0	97.43	98.54	99.66
0.1	99.32	101.20	103.09
0.5	100.97	101.74	102.51
1.0	100.32	101.91	103.49
5.0	102.93	104.45	105.96
10.	101.32	102.69	104.06
20	102.6	104.22	105.75

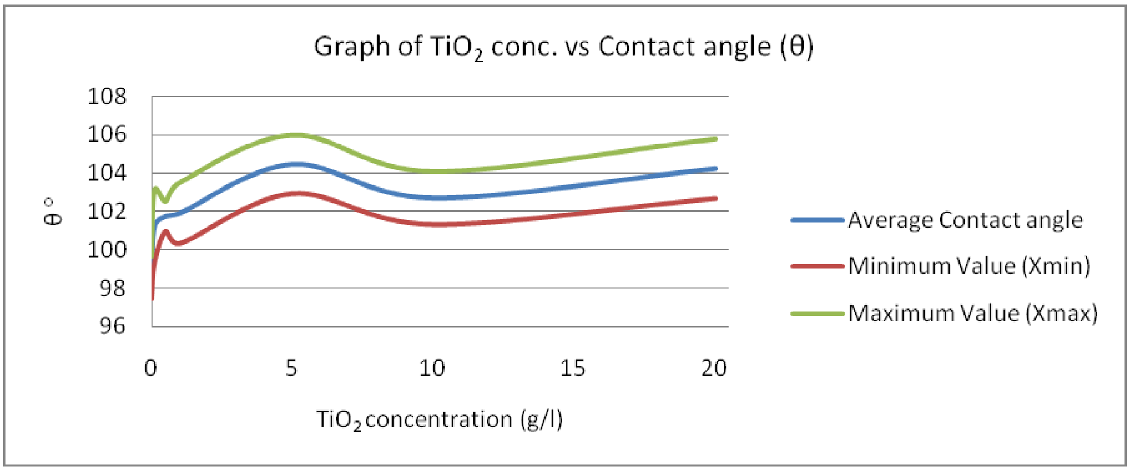


Figure 40 Description of the relation between the Contact angle and TiO_2 concentration

In this graph the most interesting part is the highest distribution at 5g/l and a a slight decrease from 10-15g/l followed by an increase at the concentration 20g/l.

Table 35 Results for TiO_2 powder with Commercial name KATI 61

TiO_2 concentration (g/l)	Minimum value (X_{min})	Average Contact angle (θ°)	Maximum value (X_{max})
0	97.43	98.54	99.66
0.1	102.54	103.56	104.58
0.5	103.01	104.30	105.58
1.0	101.98	104.01	106.05
5.0	103.80	104.63	105.46
10.	103.63	104.87	106.12
20	103.68	104.65	105.63

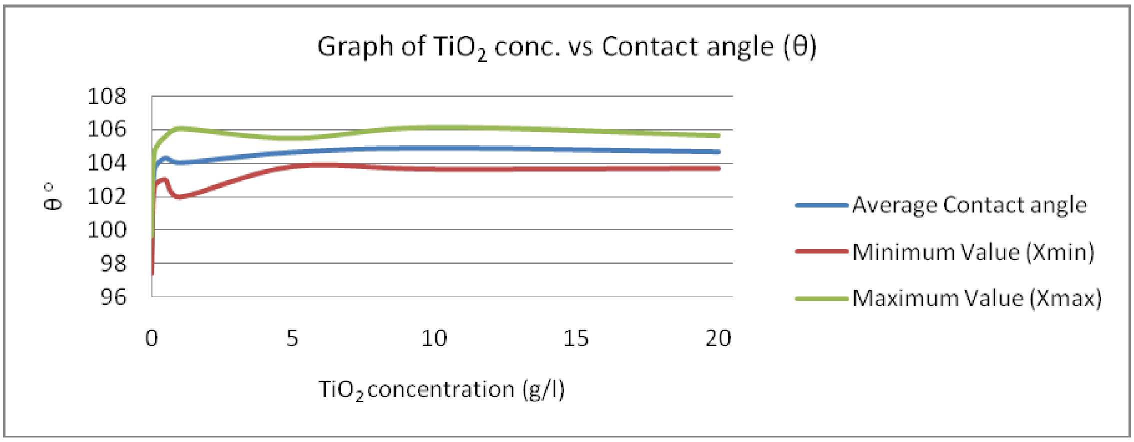


Figure 41 Description of the relation between the Contact angle and TiO_2 concentration

The observation in this graph are a little bit different from the ones in fig41, as an increase is at concentration 0.5g/l and then a small decrease at 5g/l followed by a little increase towards the highest concentration and the contact angle was constant after the increase.

Table 36 Results for TiO_2 powder with trade name KATI 66

TiO_2 concentration (g/l)	Minimum value (X_{min})	Average Contact angle (θ°)	Maximum value (X_{max})
0	97.40	98.54	99.66
0.1	101.51	102.52	103.52
0.5	103.22	105.31	107.40
1.0	101.75	103.87	105.98
5.0	104.60	105.92	107.24
10.	104.80	106.34	107.87
20	105.05	105.92	106.80

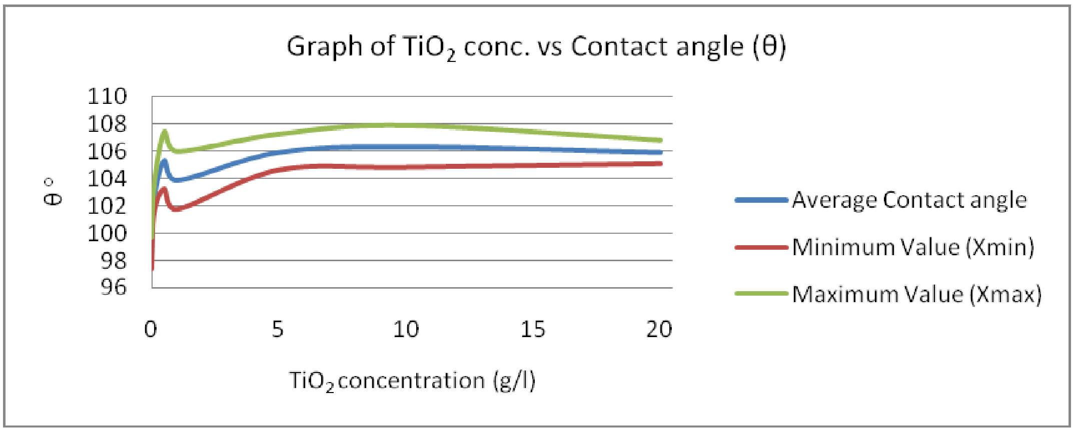


Figure 42 Description of the relation between the Contact angle and TiO_2 concentratio

Same resulting graph as in fig42,at 0.5g/l an increase followed by an increase as the concentration increases.

5.3 Results for measured UPF values

5.3.1 Sol gel treatment

5.3.1.1 The UPF values for cotton treated with different TiO2 powders

Table 37 Data showing the UPF values of cotton

TiO_2 powders	091009/1	181109/2	KATI 61	KATI66
Concentration (g/l)	UPF	UPF	UPF	UPF
0	13.78	13.78	13.78	13.78
0.1	24.01	40.5	31.03	23.68
0.5	24.35	36.42	67.76	24.63
1	27.52	37.38	82.13	22.07
5	42.5	45.92	102.44	27.22
10	131.86	125.92	214.86	14.21

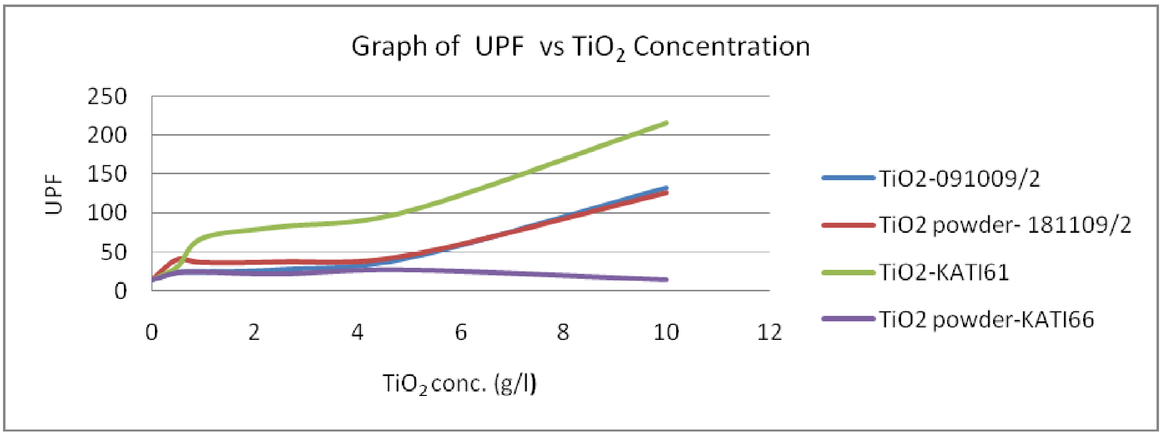


Figure 43 the UPF values of different TiO_2 powders on cotton

In comparing the UPFs values of treatment with different TiO2 powder, the graph above show the same properties for each TiO2 powder as the UPF increases with increasing TiO2 concentration. The highest UPF value observed for this material was with the TiO2 powder KATI61, lowest was with the KATI66 which possess a decrease as the concentration increases.

5.3.2Hydrophobic treatment

5.3.2.1 The UPF values of cotton treated with different TiO2 powders

Table 38 Data showing UPF values of cotton

TiO_2 powders	091009/1	181109/2	KATI 61	KATI66
Concentration (g/l)	UPF	UPF	UPF	UPF
0	25.67	25.67	25.67	25.67
0.1	31.25	27.75	32.19	37.41
0.5	43.44	29.7	26.57	28.72
1	42.54	47.04	38.68	44.39
5	210.7	26.97	231.62	135.55
10	305.05	274.87	161.12	299.84
20	388.02	881.92	536.44	1001.34

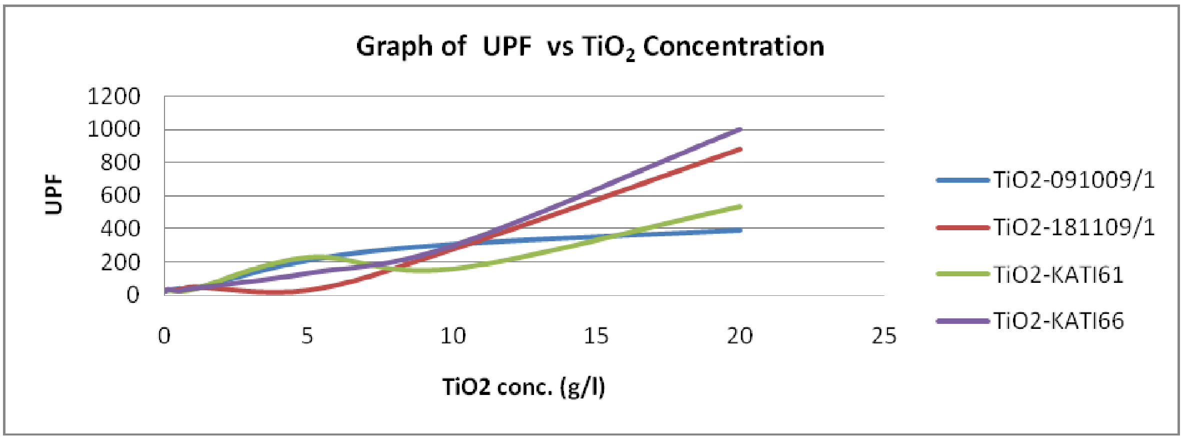


Figure 44the UPF values of different TiO_2 powder on cotton

The same observations as in fig 43, the difference is that TiO_2 is showing the highest UPF value as compared to in fig43, but the UPF is increasing in both cases As the concentration increases. The TiO_2-091009/1 has the lowest UPF value as compared to the others.

5.3.2.2 The UPF values of glass fibers treated with different TiO_2 powders

Table 39 Data showing UPF values of glass fibers

TiO_2 powders	091009/1	181109/2	KATI 61	KATI66
Concentration (g/l)	UPF	UPF	UPF	UPF
0	11.16	11.16	11.16	11.16
0.1	17.04	17.41	34.84	44.01
0.5	94.96	20.32	20.7	27.12
1	27.31	30.54	44.42	64.85
5	259	20.81	278.12	492.01
10	940.27	601.74	664.5	2254.11
20	743.1	1212.62	1913.67	4121.51

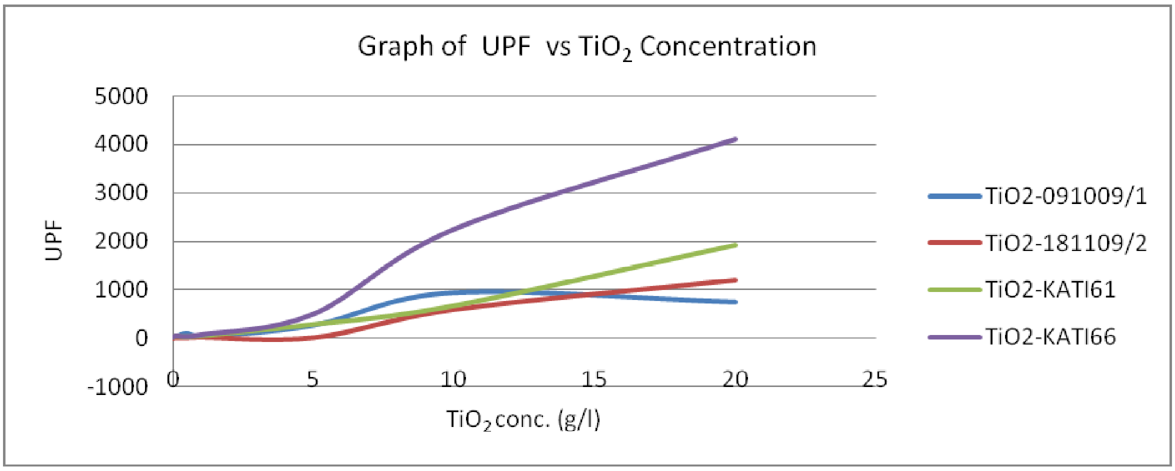


Figure 45 the UPF values of different TiO_2 powder on glass fibres

Same observation as in fig44 was the highest UPF is observed with TiO2-KATI66 and the lowest with TiO_2-091009/1.

5.3.2.3 The UPF values of Kevlar smooth surface treated with different TiO2 powders

Table 40 Data showing UPF values of Kevlar smooth surface

TiO_2 powders	091009/1	181109/2	KATI 61	KATI66
Concentration (g/l)	UPF	UPF	UPF	UPF
0	76.02	76.02	76.02	76.02
0.1	48.44	67.93	105.38	70.27
0.5	80.85	177.52	79.76	96.51
1	61.16	161.62	76.48	87.25
5	78.47	70.43	61.07	60.45
10	286.12	53.9	74.75	94.89
20	85.35	115.99	77.39	138.61

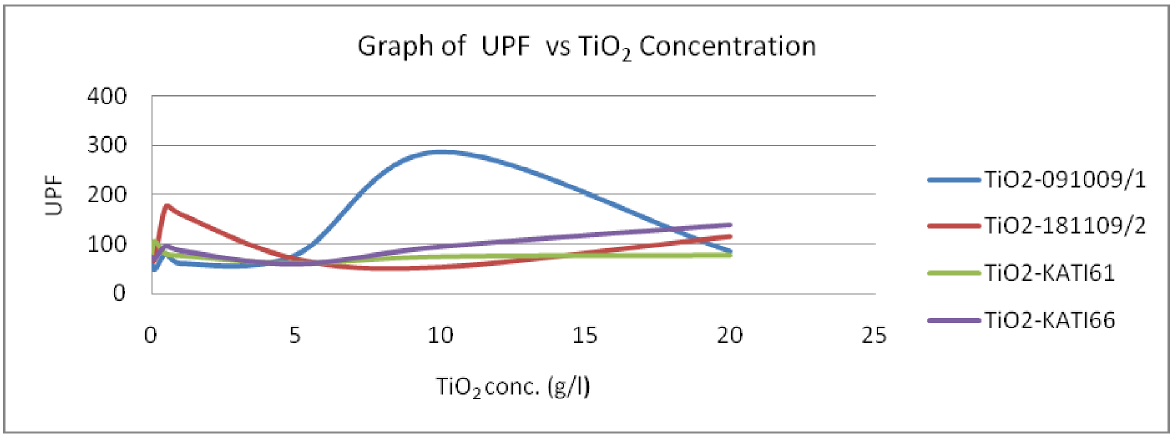


Figure 46 the UPF values of different TiO_2 powder on Kevlar smooth surface

In this graph a different observation is obtained as the three TiO_2 show an increase but not high one, more or less the same for each except for the TiO_2-091009/1 which shows the highest UPF value at concentration10g/l followed by a decrease as the concentration increases.

5.3.2.4 The UPF values of polyester treated with different TiO_2 powders

Table 41 Data showing UPF values of polyester

TiO_2 powders	091009/1	181109/2	KATI 61	KATI66
Concentration (g/l)	UPF	UPF	UPF	UPF
0	30.32	30.32	30.32	30.32
0.1	20.06	21.25	13.42	22.55
0.5	18.06	23.83	22.87	27.57
1	16.26	19.91	18.45	21.29
5	19.62	26.89	18.87	24.12
10	22.45	25.83	20.3	46.04
20	22.87	24.04	24.97	21.25

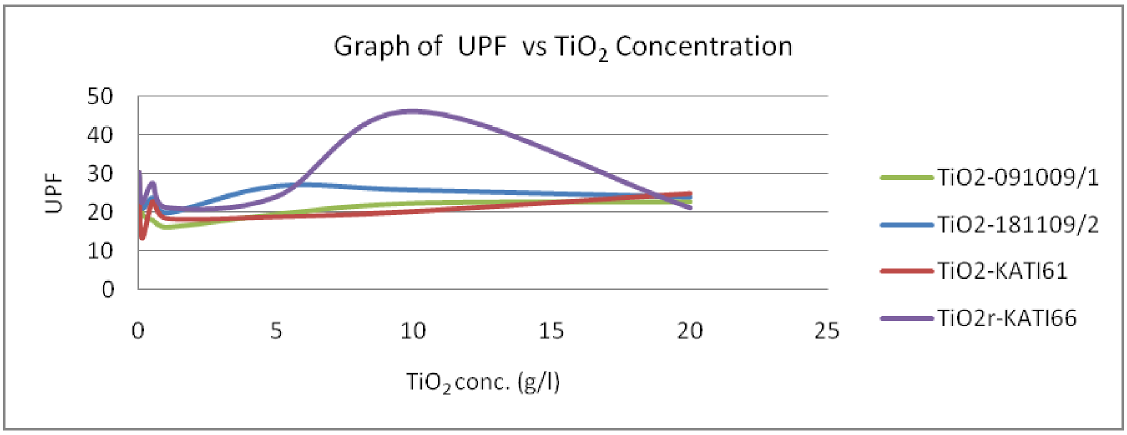


Figure 47 the UPF values of different TiO_2 powder on polyester

The same properties are observed as in fig 46, the difference is that TiO_2-KAT66 is showing the graphical distribution different from other, as it possess the highest UPF value at concentration 10g/l and a decrease as the concentration increases.

5.3.2.5 The UPF values of wool treated with different TiO_2 powders

Table 42 Data showing UPF values of wool

TiO_2 powders	091009/1	181109/2	KATI 61	KATI66
Concentration (g/l)	UPF	UPF	UPF	UPF
0	21.08	21.08	21.08	21.08
0.1	18.01	26.16	16.26	23.68
0.5	22.65	17.6	20.25	31.67
1	19.56	22.29	21.49	18.18
5	30.82	16.24	22.47	21.76
10	33.65	19.79	28.47	28.48
20	21.58	24.47	29.87	11.16

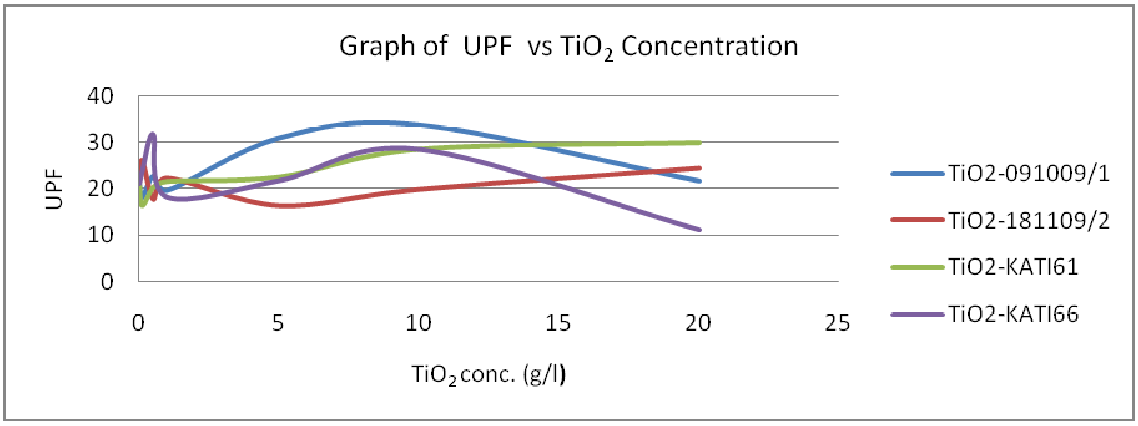


Figure 48the UPF values of different TiO_2 powder on wool

The effect of this TiO_2 powder for wool material is shown to be different as compared to the other textile materials. As it is seen on this graph above the TiO2-091009/l and TiO2-KATI have the same properties showing the highest UPF value at concentration 10g/l followed by a decrease as the concentration increases. Whereas the TiO2-181109/2 and KAT61 show different properties. The two powders show an increase in UPF values as the TiO_2 concentration increases.

5.4 Results for measured porosity of fibers

Table 43 Parameters measured during image analysis

Measured parameters	Cotton	Glass fibre	Kevlar rough surface	Kevlar-smooth surface	Polyester	Wool
Mean threshold	113.4	165.1	116.6	144.5	127.5	127.5
covering %	99.9	91.6	86.4	81.7	96.2	94.5

5.4.1 The images analyzed for the porosity measurement for Cotton, Glass fiber, Kevlar rough surface, Kevlar smooth surface, polyester and wool

The porosity of fibers was determined using image analysis using the Mat LAB software and the following images show the results before analysis and results after analysis. The images were described as follows:

A-Gray image

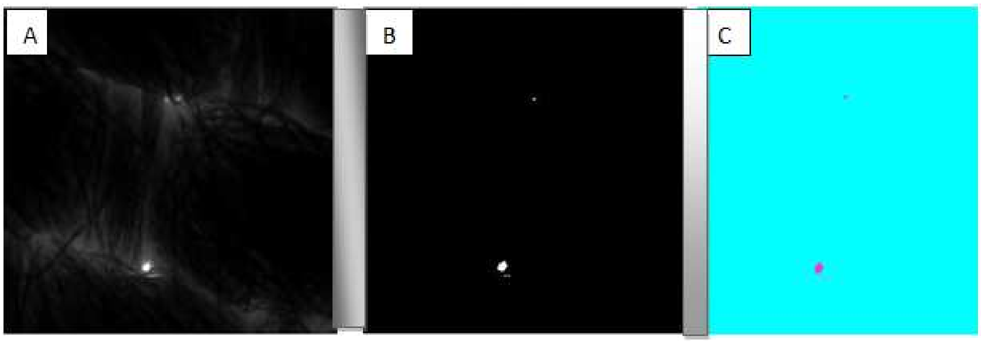
B-Binary image The covering of all fibres was determined from the mean, standard deveiation

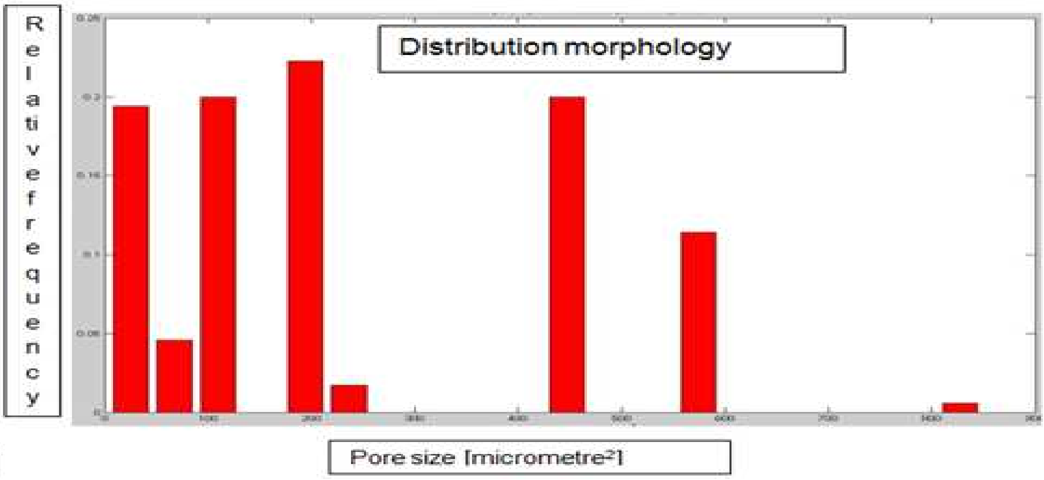
C-RGB colors

The gray images are derived images with values of image point in the range of 0-225. The gray images are transformed by the system from the RGB images. The binary images have 2 value pixels [0 -background and 1-objects and structures]. These binary images are the product of segmentation of RGB or gray scale.

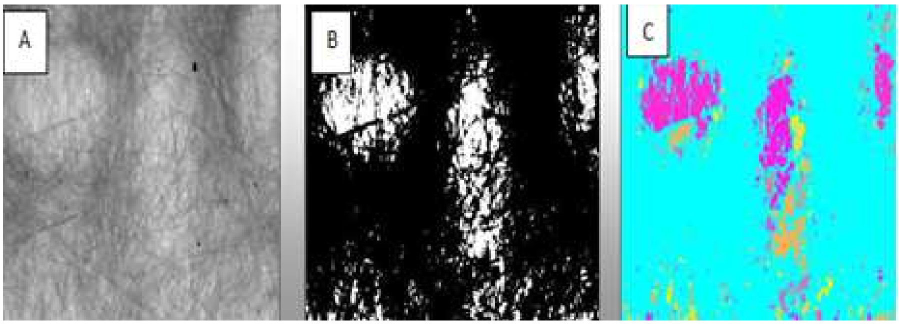
The RGB images describe three components intensity of red, green and blue. The value s of pixels for each component is in range of 0-255. This RGB images describes the intensity and shade measurement.

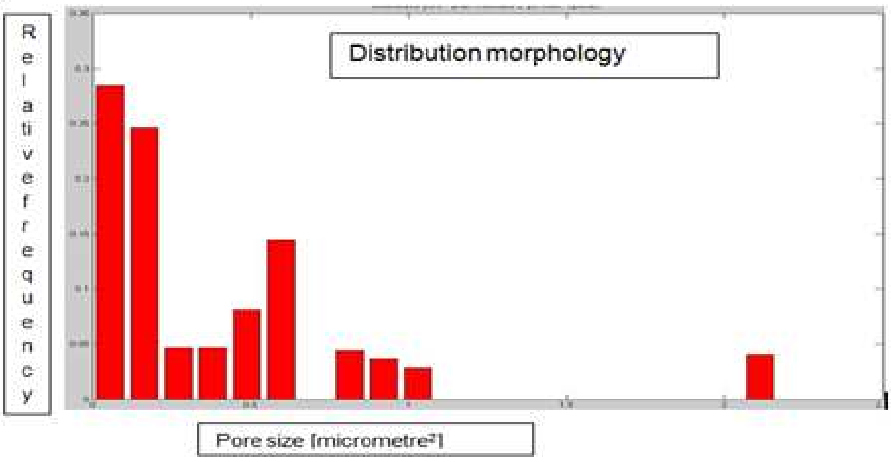
Cotton



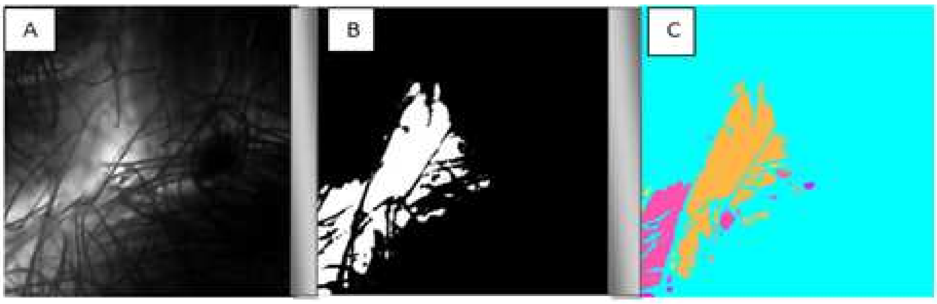

Relative frequency
Distribution morphology
Pore size [micrometre²]

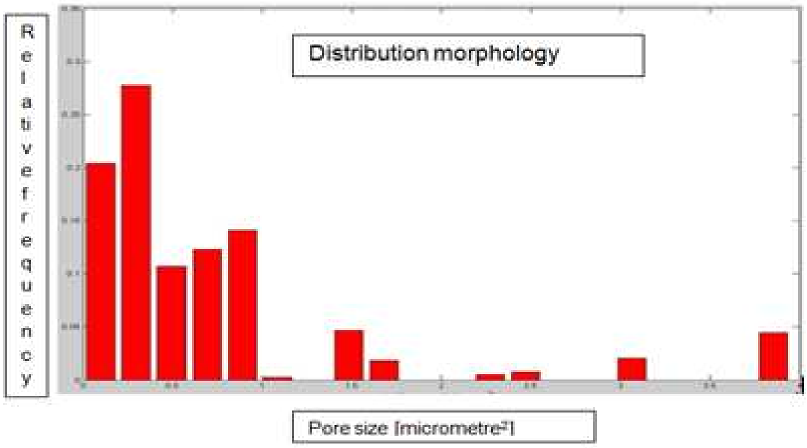
Glass fibre


A
B
C

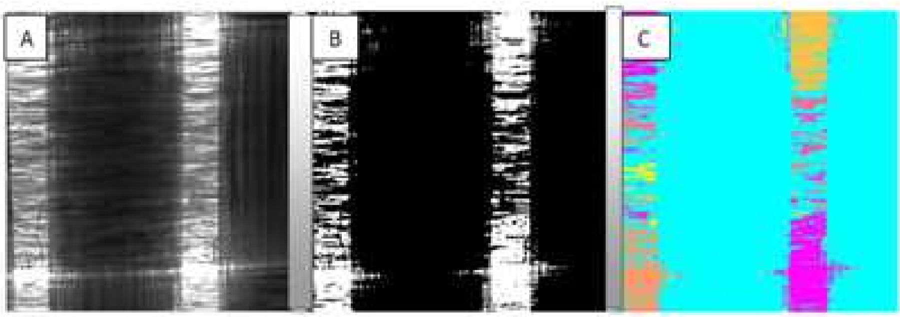

Relative frequency
Distribution morphology
Pore size [micrometre²]

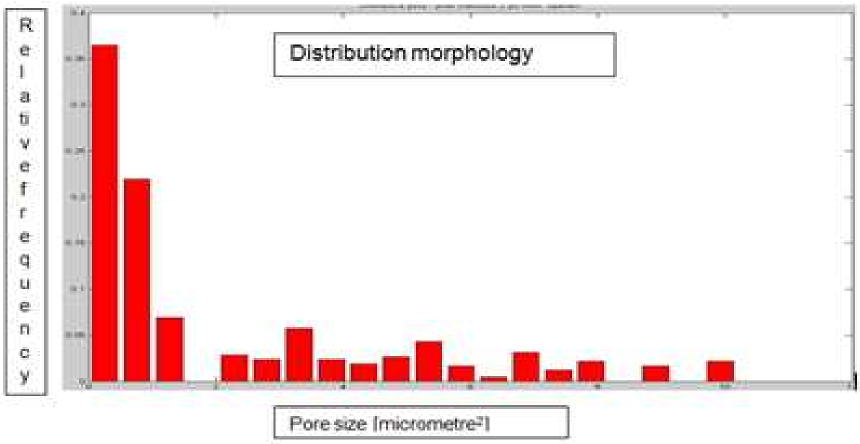
Kevlar rough surface



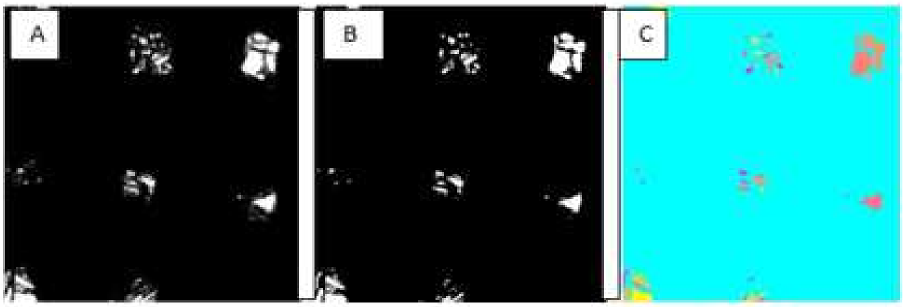


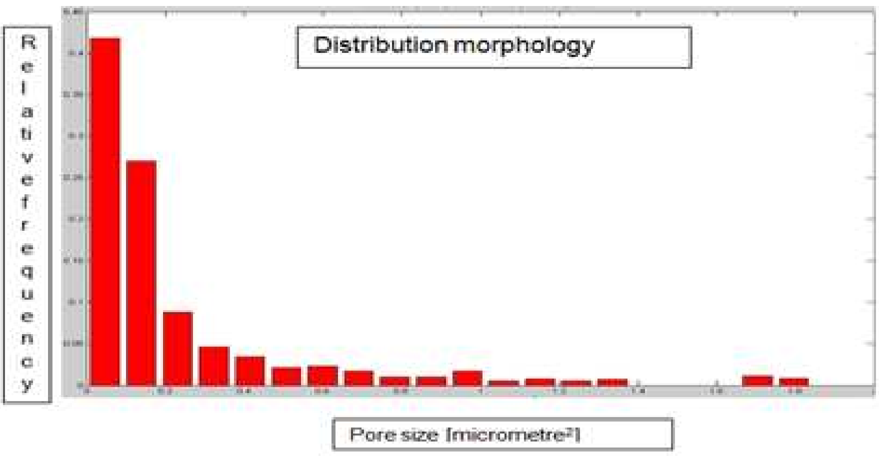
Kevlar ***smooth*** *surface*



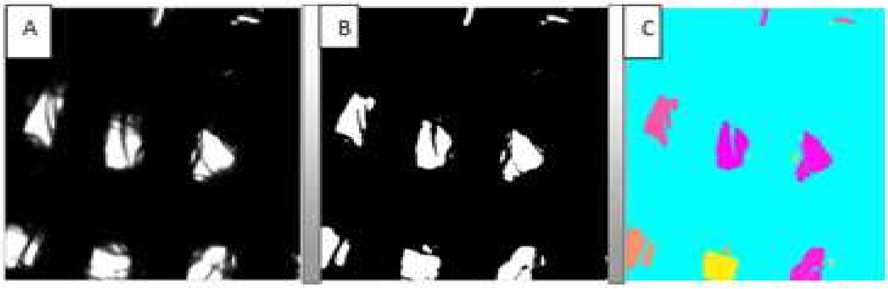


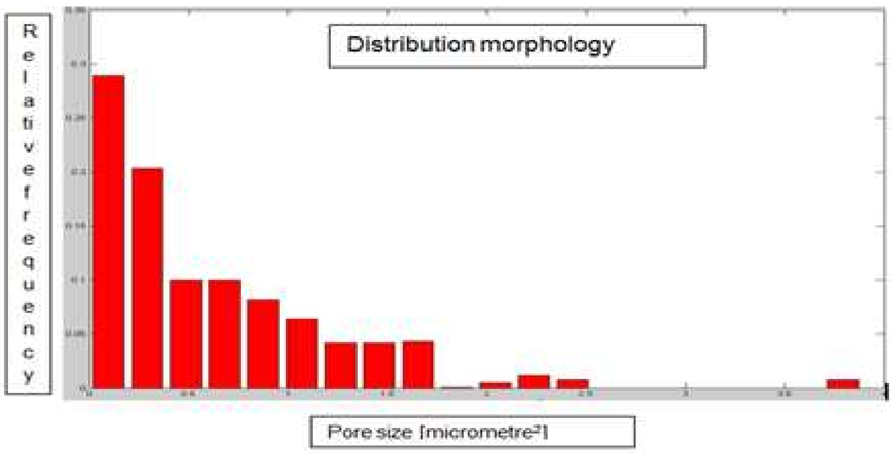
<u>Polyester</u>





Wool


A
B
C


Distribution morphology
Relative frequency
Pore size [micrometre²]

6 Discussion

The purpose of the contact angle measurement is to study the surface wettability of the textiles materials as it was on the objectives in this research work. As it is known from theory that some fibers are more hydrophilic than others, for examples cotton substrates, had the contact angle for original cotton was 0°, because water drops spread instantly when placed on the surface of the substrate. This is due to the cellulose hydroxyl groups of cotton that make cotton super-hydrophilic. But after treatment with sol-TiO_2 and application hydrophobic finish the cotton substrate showed an increasing of contact angle of above 90º as the concentration of the $_{TiO2}$ increases. As it known in theory that a surface with a contact angle of 0º to 30º has hydrophilic property whereas a surface with contact angle 90º and more is super-hydrophobic. The application of sol-TiO_2 finish and hydrophobic finish with TiO_2 nanoparticles on the textile material surface show an improvement in surface properties of the textiles making the surface more rough because of the layer on the surface of the material. This improves the wettability properties of the textile material, and thus increases the contact angle of the material. This are the finding observed in this research work, as it is observed from the graphs obtained for comparing the contact angle with this TiO_2 concentration of different textile materials. The overall observations for the contact angle measurement was that TiO_2 nanoparticles have an effect on the surface textile material as applied finishing methods, and that its effect increases the surface wettability of the textile material. The degree of increase depends on the important property of materials that is controlled by the chemical composition and the geometry of the surface.

The textile UV protective shielding properties treated textiles were characterized the UV-VIS spectrophometry. The Ultraviolet protection factor was determined during the research. When radiation strikes the textile material or any objects it can be reflected, absorbed or transmitted through the fibers of the material or space between the fibers, depending on how porous the textile is. The UPF determination strongly depends on the chemical structure of fibers. In theory the textile material with UPF>40 provide excellent protection .The UPF increases with fabric density and thickness for similar construction of textile material. The relative order of the important factors affecting the UPF values of the textiles is as follows; %cover > fibre type > fabric thickness. The fabric construction is determined by the weight and porosity of the material. The porosity is the openness or the tightness of weave in the warp and weft direction and is defined in percentage. The UV transmission through the fabric is determined by the porosity of the fabric, for example if the fabrics have maximum value of yarns in warp and weft the UPF becomes higher. In this research the UPF values of different treated fibers was determined and the findings observed were that cotton and glass fibre showed an increase in UPF values from low TiO_2 concentration to higher concentration. The glass fiber had the highest UPF value of 4000 and cotton for hydrophobic treatment was 2000, for sol gel was bout 200. The UPF value depends on how porous the structure of the material and the less porous the higher the UPF values. For Kevlar, and polyester the UPF values were low compared to glass and cotton, and they also showed the same characteristics of an increasing with an increase in concentration. The highest UPF value obtained for polyester was about 45 and for Kevlar were about 300. Fibers like Kevlar are very sensitive to UV radiation, if expose to UV the fibre' strength decrease and also changes its color. From the results obtained it is observed that finishing treatment increased the UV protective properties of Kevlar, as it had a maximum UPF value of about 300. For wool material the UPF value was lower than the rest of the fibers, the maximum UPF value observed from results was about 30. As mentioned before the UPF values of textile depends on the how porous the textile is, so this indicates that wool has poor or less protective properties against UV, this might be due to the large spaces between fibers in the warp and weft direction of the wool structure. The UPF values for Kevlar-rough surface was not measured due to that the Kevlar samples was not able to transmit light, that is the light transmitted through the sample was equal to zero. For the porosity measurement of textile, image analysis system was used and also the morphology distribution between pores of fibers was observed by the histogram above, for all fibers used.

The morphology operations involve dilation, erosion, open and close of binary image. After dilation the objects are enlarged, the outer layer of objects is added. If the distance between two objects is shorter than the thickness of two layers these objects are connected together. After erosion the objects are shrunk, the inner layer of the object is subtracted. If an object is thinner than the thickness of the inner layer this disappears from the image. For open binary images the erosion is followed by dilation , the size of objects is not significantly affected. Contours are smoothed, small objects are suppressed and gently connected, particles disconnected. For close binary images the dilation is followed by erosion were the size of objects is not significantly affected. Contours are smoothed; small holes and small depressions are suppressed. Close objects may be connected together. The morpholy distibution of pores is observed for all textile materials. The covering of all textiles was determined refere to table 43. From the covering the porosity of materials can be determined by using differentiating the covering from 100%,for example the covering of cotton (refere table 43) was 99.9% and from this the porosity can be found to be 0.1%.

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7 Conclusion

Super hydrophobic textile materials have been successfully prepared. The incorporation of TiO_2 particles by Titania sol finishing can not only cause a dual-size surface roughness for enhancing the hydrophobicity but also result in good UV-shielding property. All graphs for contact angle measurement show an increasing in contact angle from the lower concentration of TiO_2 to higher concentration.

The UPF values increase with increasing TiO_2 concentration for cotton, glass fiber, Kevlar and polyester, decrease in concentration for wool material. Textile materials with UPF>40 provide excellent protection, and from research work the textile material treated show very high UPF values except wool which has a UPF value less 40. The porosity of textile material determines the UV transmission through the material, the high the porosity, the higher levels of UV radiations transmission and the less UPF values.

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